Analytical Abstracts

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

4238. Developments in the analytical service given to industrial atomic energy. F. J. Woodman, T. G. Clinton, W. Fletcher and G. A. Welch (U.K.A.E.A., Risley, Lancs.). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva 1958, Rep. A/CONF.15/P/1453, 31 pp.—Some of the advances in reducing the time for analytical work which have been effected as a result of development work carried out in the analytical laboratories of the Industrial Group of the U.K.A.E.A. are described. Continuous uranium monitors for raffinates based on a solvent extraction separation and an absorptiometric finish and for process streams based on "in line" γ-absorption measurement are discussed. For laboratory application, the instruments and techniques described include—a direct-reading high-resolution spectrograph for U isotopic analysis; adaptations of instrumental techniques under high activity conditions; the use of γ-spectrometry for rapid, specific determinations on large numbers of biological samples; the use of gas chromatography in the analysis of corrosive gas mixtures.

NUCL. SCI. ABSTR.

4239. o-Dithiols in analysis. VIII. Use of the zinc complex of toluene-3:4-dithiol in the field-testing of ores and minerals. R. E. D. Clark and C. E. Tamale-Ssali (Dept. of Sci. and Technol., Tech. Coll. and Sch. of Art, Cambridge, England). *Analyst*, 1959, **84**, 16–23.—The zinc complex of toluene-3:4-dithiol is recommended as a reagent for testing for Cu, Ag, Au, Zn, Sn, Pb, V, As, Sb, Bi, Mo, W, S (free), Se, Te, Mn, Fe, Co and Pt in their ores and minerals. Almost all the tests described can be carried out on the coarsely crushed ore in 30 to 60 sec., except those for the noble metals (2 to 3 min.). The tests are suited to field conditions. Filtration, when necessary, is effected by forcing a cotton-wool plug through the liquid, the clear liquid above the plug being removed by pipette. If the solid is required, the plug is washed with water by the same procedure, then dried, and the test is applied directly to the enmeshed solid. The preparation of Zn-free dithiol for use in tests for Zn is described. Interferences are rare and can usually be avoided. A. O. JONES

4240. Dithio-oxamide as a colorimetric reagent in the detection of metal ions. Samir K. Banerji and Arun K. Dey (Univ., Allahabad). *J. prakt. Chem.*, 1958, **6**, 62–64 (in English).—Two or three drops of a 0·1% soln. of dithio-oxamide in alcohol were added to 1 ml of a 0·1 M soln. of the metal salt in acid, neutral or alkaline soln. Sensitive colour tests were obtained with Cu^{2+} (olive green), Ni^{2+} (violet), Zr^{4+} (violet in alkaline soln.), and Co^{3+} (brown in acid and neutral soln., black - green in alkaline soln.). A violet - blue colour was obtained with $K_2Cr_2O_7$. CHEM. ABSTR.

4241. Use of sulphathiazole in inorganic analysis. Yu. D. Gnesin. *Uch. Zap. Pyatigorsk. Farmatsevt. Inst.*, 1957, **2**, 283–295; *Ref. Zhur., Khim.*, 1959, (3), Abstr. No. 7960.—The reactions of Cu^{2+}, Ag^+, Hg^{2+}, Hg_2^{2+}, Bi^{3+} and Co^{2+} with sulphathiazole are studied. The detectable minima (in μg) and limiting dilutions for these ions are—Cu^{2+}, 0·075 (1 in $1·3 \times 10^7$) at pH 1·2; Ag^+, 0·085 (1 in $1·1 \times 10^6$) at pH 4·6; Hg_2^{2+}, 0·07 (1 in $1·4 \times 10^6$) at pH 4·2 to 4·6; Hg^{2+}, 0·073 (1 in $1·3 \times 10^6$) at pH 7·8 to 8·0; Bi^{3+}, 0·43 (1 in $2·3 \times 10^5$) at pH 4·72 to 4·98; and Co^{2+}, 0·1 (1 in 1×10^6) at pH 1·6 to 1·8 or 4·4 to 5·6. The composition and properties (m.p., behaviour on heating, and solubility in acids, alkalis and organic solvents) of the resulting compounds are studied. The structural formulae are derived from the metal contents determined.

C. D. KOPKIN

4242. Gallein as an analytical reagent. I. Lead galleinate, its composition and analytical applications. Ping-Shih T'ien and K'uei Wang. *Acta Chim. Sinica*, 1958, **24** (6), 407–412.—Gallein forms a blue coloration or ppt. with lead ions; the sensitivity is 0·2 μg, and Cu, Ce, Sb, Sn^{II} and Sn^{IV} interfere. The composition of the lead galleinate formed was determined by heterometric titration and by the slope-ratio method. The ratio of reagent to lead in the compound formed in an alcoholic medium was found to be 2:3, while in an aq. medium of pH 8 it was 1:1. Gallein may be used as the reagent in the heterometric titration of lead and in its colorimetric determination. Large amounts of other salts impair the determination. Beer's law is obeyed in the concn. range 5 to 150 μg of Pb per 10 ml. Gallein may also be used in the standard colorimetric series for the visual colorimetric determination of lead. SCI. ABSTR. CHINA

4243. Simple method for recovering molybdenum from molybdenum-containing filtrates from phosphoric acid determinations. H. Dietrich and P. von Polheim (Staatl. Landwirtschaftl. Versuchs- und Forschungsanst, Augustenberg, Post Grötzingen bei Karlsruhe, Germany). *Z. anal. Chem.*, 1959, **166** (1), 18–23.—The recovery of 85 to 90% of the Mo as pure ammonium molybdate fit for immediate use in phosphate determinations can be achieved by the proposed method. The filtrate is neutralised with aq. NH_3 and the Mo is pptd. from the boiling soln. with the calculated amount of ammonium phosphate. The soln. is set aside overnight and the ppt. is filtered off and washed with H_2O. The ppt. is dissolved in aq. NH_3 and sufficient $MgCl_2$ is added to precipitate the P. When the filtered soln. is made just acid with acetic acid, ammonium molybdate crystallises out overnight.

G. BURGER

4244. Notes on perchloric acid and its handling in analytical work. Analytical Methods Committee, Society for Analytical Chemistry. *Analyst*, 1959, **84**, 214–216.—In this report, prepared by the Metallic Impurities in Organic Matter Sub-committee, the circumstances in which the use of $HClO_4$ in analytical work and its storage under laboratory conditions may involve danger are described, and routine safeguards in laboratory practice to minimise or remove such danger are suggested.   A. O. JONES

4245. Analytical application of -onium compounds. XII. Tetramethylammonium phosphate buffer and its polarographic application, with some notes on the carbon dioxide effect. Mutsuaki Shinagawa, Hiroshi Matsuo and Nobuko Okamoto (Univ., Hiroshima). *J. Sci. Hiroshima Univ., Ser. A*, 1957, **21**, 131–137.—The use of the buffer as a supporting electrolyte at negative potentials is described. Its max. buffer capacity is at pH 6·9. An obstructive wave, formed at $-2·0$ to $-2·4$ V, is believed to be due to the formation of methyl carbamate by CO_2. Boiling or treating the buffer soln. with an anion-exchange resin eliminates the wave.   CHEM. ABSTR.

4246. Separation of bivalent from tervalent cations in the presence of phosphate by a modified ammonia method, and comparison with separation by the urea method. F. Krleža (Lab. of Anal. Chem., Philosoph. Fac., Univ., Sarajevo, Yugoslavia). *Croat. Chem. Acta*, 1958, **30** (4), 231–235 (in English).—The separation of Mg, Ca, Sr and Ba from Al, Cr or Fe can be achieved by pptg. the tervalent ions from a soln. containing NH_4NO_3 and enough aq. NH_3 to give a pH of 6·9 to 7·0. The maximum proportion of phosphate allowable before co-pptn. of the bivalent ion occurs has been determined, and is less than for the urea method. For a given tervalent ion, the upper permissible limit of phosphate content falls from Mg to Ba, i.e., in the order of decreasing solubility product of the secondary phosphate of the bivalent ion. For a given bivalent ion, the upper permissible limit of phosphate content falls in the order Al, Fe, Cr, i.e., in order of increasing solubility product of the tervalent metal phosphate. *Procedure*—Dissolve 10 g of NH_4NO_3 in 80 ml of water and boil. Add sufficient freshly distilled aq. NH_3 (1 to 9) to give a pH of 6·9 to 7·0 in the final soln. To the hot soln. add dropwise 50 ml of test soln. Cover the beaker and set aside for 20 min. at 60°, washing the ppt. three times by decantation with 100-ml portions of 0·5% aq. NH_4NO_3 soln. Allow to cool to room temp. Measure the pH of the soln. and filter off the ppt. Determine the bivalent metal in the filtrate. Figures quoted of the results obtained indicate excellent recovery of bivalent metal within the limits of phosphate content referred to above.   H. M.

4247. Indicators for non-aqueous acid-base titrimetry. I. J. T. Stock and W. C. Purdy (Dept. of Chem., Univ. of Connecticut, Storrs, U.S.A.). *Chemist Analyst*, 1959, **48** (1), 22–28.—The literature up to June 1958 is surveyed, with 184 references. After a short discussion of the nature and history of the technique, the various procedures are briefly described, under indicator headings, giving the substance determined, titrant and solvent used. The indicators considered are azo dyes (*p*-aminoazobenzene, azo violet, methyl orange, methyl red, methyl yellow, and others less commonly used) and triphenylmethane dyes [crystal violet, methyl violet, malachite green and Victoria blue R (C.I. Basic Blue 11)].   R. E. ESSERY

4248. New applications of the diphenylamine indicator in volumetric oxygen-adsorption reactions. F. Sierra and G. Asensi. *An. Real Soc. Esp. Fis. Quim., B*, 1958, **54** (1), 13–28.—Iodide can be determined volumetrically with $AgNO_3$ in the presence of Br^- or Cl^-, and Ag^+ with Br^-, Cl^-, I^- or SCN^-, with a mixture of H_2SO_4, diphenylamine and potassium metavanadate as indicator.   CHEM. ABSTR.

4249. Analysis under ultra-violet light. I. Magdala red as a fluorescence indicator in precipitation titrations. J. Bognár (Tech. Univ. for Heavy Ind., Miskolc). *Acta Chim. Acad. Sci. Hung.*, 1959, **19** (4), 433–440 (in German).—In neutral or alkaline soln., Magdala red (C.I. Basic Red 6) is red by visible light and fluoresces yellow under u.v. light. The colour changes to violet, and the fluorescence is quenched, at a pH between 2 and 3·6. The fluorescence is also quenched by ¸the presence of Ag^+. Magdala red has been used successfully under u.v. light to indicate the end-point in the titration of halogen or SCN^- with $AgNO_3$, and in the titration of Ag^+ with NaBr or KSCN. In the determination of Ag^+, 1 ml of 1% dextrin soln. is added as a protective colloid. The indicator is used as a 0·2% aq. soln. [See also *Magyar Kém. Foly.*, 1959, **65** (3), 123.]   G. BURGER

4250. Eriochrome black T and its calcium and magnesium derivatives. H. Diehl and F. Lindstrom (Iowa State Coll., Ames, U.S.A.). *Anal. Chem.*, 1959, **31** (3), 414–418.—Eriochrome black T (C.I. Mordant Black 11) (**I**) forms only 1 to 1 compounds with Ca and Mg in the pH range 8 to 10. This and the stability constants obtained for these complexes confirmed the work of Schwarzenbach *et al.* (*Helv. Chim. Acta*, 1948, **31**, 678). The measurements were made at constant ionic strength with the crystalline dimethylammonium salt of **I** (preparation described).   G. P. COOK

4251. Polarographic behaviour of Variamine blue. E. Bányai and P. Zuman (Polarographic Inst., Acad. Sci., Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (2), 522–525 (in German).—The reversible two-electron oxidation of Variamine blue (C.I. Azoic Diazo Component 35) (**I**) to *p*-anisyl-*p*-benzoquinonedi-imine has been studied polarographically in relation to pH, with the Hg_2SO_4 reference electrode and K_2CrO_4, $K_3Fe(CN)_6$, Ce^{4+} and Fe^{3+} as oxidants. The oxidation of **I** with K_2CrO_4 and $K_3Fe(CN)_6$ is quant. at pH 4·7 or 6·8, whereas that with Ce^{4+} and Fe^{3+} is not complete in acetate medium. The oxidation of **I** in borate buffer soln. (pH 9) has been studied by the amperometric titration of **I** with $K_3Fe(CN)_6$.   J. ZÝKA

4252. Photometric determination of indicator end-points in complexometric titrations. Sôichirô Musha, Makoto Munemori and Kin'ya Ogawa (Appl. Chem. Dept., College of Engng, Univ. of Osaka Prefecture, Sakai, Osaka). *Bull. Chem. Soc. Japan*, 1959, **32** (2), 132–137 (in English).—The utility and limitations of a graphical method (Musha *et al.*, *Ibid.*, 1957, **30**, 675) for determining the end-point in complexometric titrations by a photometric technique are discussed with respect to the titration of Mg and Ca with EDTA (disodium salt), with Eriochrome black T as indicator, and of Ca with murexide as indicator.   I. JONES

4253. Composition of a tetra-alkylammonium base titrant. M. L. Cluett (E. I. du Pont de Nemours & Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 610–611.—The strongly basic titrant prepared by the reaction of tetra-*n*-butyl-ammonium iodide with Ag_2O in anhyd. methanol has been found to consist of a mixture of hydroxide and methoxide (1:1). G. P. Cook

4254. Quantitative anodic chronopotentiometry at the platinum electrode. J. D. Voorhies and J. S. Parsons (Res. Div., Amer. Cyanamid Co., Bound Brook, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 516–519.—Anodic chronopotentiometry at a straight platinum-wire electrode has been used for the determination of oxidisable organic compounds. Mercaptobenzothiazole can be determined with a relative precision of $\pm 1\%$, based on **13** assays in a concn. range of $0 \cdot 8$ to $1 \cdot 1 \times 10^{-3} M$ at two current levels. The determination of toluene-2:4-diamine has also been studied. K. A. Proctor

4255. Determination of the solubility of organic solvents in mineral acids. D. G. Tuck (Cornell Univ., Ithaca, N.Y., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (2), 159–163.—Hydrochloric acid is saturated with di*iso*propyl ether (**I**) by shaking and the excess of **I** is separated. An aliquot of the aq. layer is neutralised with NaOH soln. (25%, w/w), the liquid is centrifuged in a Babcock tube and the vol. of **I** that separates is read on the previously calibrated neck of the tube. A correction for the solubility of **I** in the salt soln. is determined. The solubility of **I** in aq. HCl rises sharply when the concn. of the acid exceeds 7 M. H. N. S.

4256. Applications of extraction in inorganic analysis. A. K. Babko and F. G. Zharovskiĭ. *Zavod. Lab.*, 1959, **25** (1), 42–52.—A review is presented, with **166** references. G. S. Smith

4257. Infra-red analysis of solid substances. A review. G. Duyckaerts (Univ. of Liége, Belgium). *Analyst*, 1959, **84**, 201–214.—The physical and chemical factors affecting the i.r. spectra of solid substances are reviewed. Among the physical factors discussed are the influence of the dimensions of the individual absorbing particles and of differences in refractive index between the solid absorbing substance and the dispersing medium (liquid paraffin, KBr, etc.). The chemical influences discussed include the adsorption of the substance on particles of the dispersing medium, the chemical reaction or complex-formation of the substance with the medium, the polymorphism of the substance, mixed crystal formation and distortion of the crystalline structure. (23 references.)

A. O. Jones

4258. The method of oscillographic polarography in chemical analysis. J. Doležal and J. Zýka (Inst. Anal. Chem., Charles' Univ., Prague). *Öst. Chem-Ztg*, 1959, **60** (7), 189–196.—Applications of oscillographic polarography are reviewed and the apparatus used is described.

4259. Radioactivity applied to analytical chemistry. H. Götte (Max Planck Inst. f. Chem., Mainz, Germany). *Técnica, Lisbon*, 1959, **34**, 525–535.—A review with 9 references.

4260. Radiochemical investigations on the recovery for analysis of trace elements in organic and biological materials. Report to the Analytical Methods Committee. T. T. Gorsuch (Radiochem.

Centre, White Lion Rd., Amersham, Bucks., England). *Analyst*, 1959, **84**, 135–173.—The radiochemical methods used involve the final determination of radioactive isotopes either added as tracers or formed by irradiation of the sample. Since any of the elements extraneously introduced during the analysis will be inactive, measurement of the radioactivity of the separated element will be a true indication of the loss of the element caused by the conditions of the analysis. Also, adsorption of the element by co-pptn. or by the apparatus can be located and measured. For stated reasons, cocoa was generally used as the sample and the investigation was then extended to some other materials. The recovery of the following elements under various conditions of analysis was investigated —Pb, Hg, Zn, Se, As, Cu, Co, Ag, Sb, Cr, Mo, Sr and Fe. A. O. Jones

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

4261. Reductimetric determination of metals in non-aqueous media. J. Minczewski, S. Kołyga and L. Wódkiewicz (Polish Acad. Sci., Warsaw). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/1596, 8 pp.—Chromous acetate in dioxan soln. was used as a reducing agent in non-aq. media. The method was applied to the determination of uranyl nitrate in a soln. of ethanol and to the determination of Cu and V after extraction with a soln. of 8-hydroxyquinoline in $CHCl_3$. Good reproducibility and accuracy were obtained in concn. of $\simeq 0 \cdot 2$ mg per ml.

Nucl. Sci. Abstr.

4262. Indirect ascorbimetric determination of strong oxidising agents. L. Erdey, I. Buzás and K. Vigh (Inst. f. Allg. Chem., Tech. Univ., Budapest). *Period. Polytech.*, 1959, **3** (1), 1–15 (in German).—Chlorite, ClO^-, BrO^-, $S_2O_8^{2-}$, $Cr_2O_7^{2-}$, MnO_4^-, Cl, Br and H_2O_2 can all be determined by adding an excess of Fe^{II} salt and titrating the Fe^{III} formed with standard ascorbic acid. Nitrites may be titrated potentiometrically with ascorbic acid in an acetate buffer at pH 4.

T. R. Andrew

4263. Separation of zinc, lead and copper on an anion-exchange resin. M. N. Zvereva and V. N. Shibarov. *Vestn. Leningr. Univ.*, 1959, No. 4, *Ser. Fiz. i Khim.*, (1), 145–148.—Copper, Zn and Pb were separated quant. by means of anion-exchange resins PE-9 and EDE-10 "P." The air-dried anionite (6 g) was supported in a column $1 \cdot 0$ to $1 \cdot 5$ cm in diam. and the exchange carried out in $CHCl_3$. Separation was commenced with 2 N HCl (100 ml) which rapidly removed the Cu but left the Pb and Zn complexes on the column. Zinc was then removed with $0 \cdot 3$ N HCl, and Pb with H_2O. The tabulated results indicate that the accuracy of determination of Cu, Zn and Pb is not greater than that of the usual analytical procedures.

K. R. C.

**4264. Use of tiron for the chromatographic separation of iron, aluminium, titanium, tin and antimony from calcium, magnesium, zinc and

copper. I. R. N. Golovatȳĭ. *Ukr. Khim. Zhur.*, 1958, **24** (5), 653–655; *Ref. Zhur., Khim.*, 1959, (11), Abstr. No. 38,274.—The method described is based on the formation of complexes of Fe^{3+}, Al^{3+}, Sb^{3+}, Sn^{4+} and Ti^{4+} with tiron (**I**), which are not decomposed when the soln. is passed through a column of cationite SBS in the NH_4^+ form. The complexes of Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+} and Cu^{2+} are less stable, and these cations are retained on the resin. *Procedure*—Treat the test soln. with sufficient $0·05\,M$ **I** to complex Fe^{3+}, Al^{3+}, Sb^{3+}, Sn^{4+} and Ti^{4+} completely. If the soln. contains Sb^{3+} or Sn^{4+}, the formation of the complexes is accelerated by heating to boiling-point. Then add aq. NH_3 to the soln. till the blue colour of the complex of Fe^{3+} with **I** changes to red (pH >8); if the soln. does not contain Fe, a small amount is added. After adjusting the pH, dilute the soln. to between 120 and 150 ml and pass it through the column at a rate of 3 to 4 ml per min. Calcium, Mg, Cu, Zn and large amounts of Mn are eluted from the column with hot $3\,N$ HCl, and small amounts of Mn with cold $1·5\,N$ HNO_3. Magnesium, Zn and large amounts of Mn are determined in the filtrate with phosphate, Ca with oxalate, and Cu iodimetrically; small amounts of Mn and Cu are determined photometrically.   C. D. KOPKIN

4265. Extraction in the radiometric titration of certain cations. I. M. Korenman, F. R. Sheyanova, L. V. Gorbunova and N. K. Romanova. *Trudȳ Khim. i Khim. Tekhnol.*, 1958, (1), 109–117; *Ref. Zhur., Khim.*, 1959, (2), Abstr. No. 4289.—The use of ^{65}Zn and ^{115}Cd as non-isotopic indicators in the radiometric titration of Hg, Cu, Zn and Cd with a $CHCl_3$ soln. of dithizone (**I**) is described. Conditions are studied for the radiometric analysis of the binary mixtures Hg - Zn, Hg - Cd, Cu - Zn, and Cu - Cd, and the ternary mixtures Hg - Cu - Zn and Ag - Cu - Cd. The use of ^{65}Zn and ^{115}Cd as non-isotopic indicators for the determination of Hg and Cu enables preparations of low specific activity to be used, since they may be added to the soln. in amounts commensurate with those of the ions to be determined, and avoids the use of short-lived isotopes of Hg and Cu. For the simultaneous determination of Hg and Zn (or Cd) as the dithizonates by the radiometric method (*Ref. Zhur., Khim.*, 1958, Abstr. No. 24,729), add to a series of tubes (with ground glass stoppers) $0·5$ ml of the soln. of Hg, $0·5$ ml of a soln. of a zinc salt of known concn. labelled with ^{65}Zn (of specific activity 35 impulses per min. per μg), and add 1 ml of a buffer soln. of pH $4·7$, various amounts of a $CHCl_3$ soln. of **I**, and pure $CHCl_3$ to give a total $CHCl_3$ layer of 2 ml. Shake the contents of the tubes for 15 min., centrifuge for 1 or 2 min., and determine the activities of the aq. and $CHCl_3$ layers in each tube. By the gradual addition of the soln. of **I**, mercury dithizonate is first formed and extracted (instability const. 7×10^{-43}); the activity of the aq. and $CHCl_3$ layers remains constant. As soon as zinc dithizonate (instability const. 8×10^{-24}) or cadmium dithizonate (instability const. $2·9 \times 10^{-20}$) begins to be extracted, the activity of the aq. layer decreases, while that of the $CHCl_3$ layer increases. The total activity of equal vol. of the aq. and $CHCl_3$ layers should be constant at all points of the titration. The end-point is determined graphically or from formulae derived from the solution of the simultaneous equations of the titration curves. The concn. of the soln. of **I** is found in the same way, using known amounts of Hg and Zn. The

described procedure may be used for the determination of micro amounts of Hg. An analogous method, based on the differing stabilities of the dithizonates, permits the determination of Cu and Zn (or Cd) without a preliminary separation, and also enables a mixture of three cations to be analysed (*e.g.*, Hg - Cu - Zn and Ag - Cu - Cd); in this case use as indicators isotopes of the elements which form the least stable and the most stable complexes (*e.g.*, Hg and Zn). Satisfactory results are obtained when applying the developed procedure for the radiometric titration of two cations to the analysis of brass, duralumin and a zinc alloy (with ^{65}Zn as indicator).   C. D. KOPKIN

4266. Simple method for determination of the radiochemical purity of isotopes by means of paper electrophoresis. M. Mach (Res. Inst. of Radiology, Prague). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/2109, 10 pp.—It was found that paper electrophoresis ensures a better separation of active contaminants than paper chromatography. With the acid electrolytes $HClO_4$ or HNO_3, an absolute separation of orthophosphate, sulphate and chloride was achieved, *i.e.*, of ionic forms, in which the impurities of radio-isotopes ^{35}S, ^{36}Cl, and of irradiated chlorides as a result of production processes are present. Trace amounts of sulphates were separated from phosphates with dil. HCl as electrolyte. The separation of radio-tellurium from radio-iodine was achieved only after the oxidation of samples by using different electrolytes at the positive and negative electrodes. By using the results of Zimakov *et al.*, contaminating ruthenium was separated from Sr and Y in 2% soln. of $K_4Fe(CN)_6$ and contaminating radio-caesium from ^{90}Sr in $0·5\,N$ NaOH by paper electrophoresis. (*Cf. Anal. Abstr.*, 1959, **6**, 2403.)
                NUCL. SCI. ABSTR.

4267. Radiometric determination of thallium, silver and lead by the non-isotopic indicator method. I. M. Korenman, F. R. Sheyanova and P. V. Mulyanov. *Trudȳ Khim. i Khim. Tekhnol.*, 1958, (1), 118–124; *Ref. Zhur., Khim.*, 1959, (2), Abstr. No. 4290.—Conditions are studied for the radiometric titration of Tl with a soln. of KI, with ^{204}Tl as radioactive indicator; procedures are also described for the determination of Tl, Ag and Pb, with ^{204}Tl and ^{110}Ag as indicators. To determine Tl, add to each of several centrifuge tubes 1 ml of a soln. of a thallium salt ($4·09$ mg of Tl) containing ^{204}Tl ($0·3\,\mu g$ of Tl) of specific activity 16,000 counts per min. per μg, acidify the soln. with two drops of $2\,N$ HNO_3, add a small amount of water so that after the titration the final vol. will be $2·5$ ml, add various amounts of $0·1\,N$ KI, rub the tube walls with a glass rod, centrifuge off the ppt. of TlI, extract $0·2$ ml of the centrifugate and measure its activity. The end-point is found graphically or by the activity at two points during the titration. Completely satisfactory results are obtained in determining $0·4$ to 4 mg of Tl per ml; with smaller amounts of Tl unsatisfactory results are obtained, because of the solubility of TlI. It is shown that an analogous titration procedure may be used for the determination of Ag and Tl when present together: the activity of the test soln. remains constant during the titration of Ag and decreases with the titration of Tl. The titration of a mixture of Ag and Tl is possible with ^{110}Ag as indicator: Tl is pptd. as described above with KI soln. in tubes of a special shape, a known vol. of a soln. of $AgNO_3$ labelled with

[110]Ag is added, the soln. are mixed, and the activity of a fraction of the mother liquor is measured (with a radiometric titration of the residue). To determine Pb, to 1 ml of a soln. of $Pb(NO_3)_2$ add 0·2 ml of a soln. of the thallium salt (0·3 μg of Tl) containing [204]Tl, acidify with two drops of acetic acid and titrate with a soln. of K_2CrO_4, measuring the activity of a fraction of the centrifugate. The described method for determining Pb gives satisfactory results and is more convenient than the method in which the short-lived [212]Pb is used as indicator.   C. D. KOPKIN

4268. Induced radiation analysis for silicon, aluminium and sodium in igneous rocks. G. M. Brownell, K. Bramadat, R. A. Knutson and A. C. Turnock. *Trans. Roy. Soc. Canada, Sect. IV,* 1957, **51**, 19–31.—Rapid quant. determination of Si, Al and Na in rocks can be made by comparing the γ-activity of these rocks with that of chemically analysed rocks. The induced radiation is proportional to the mass of the elements and is measured in a scintillation counter. Coarsely crushed rock (in 300-g samples) was subjected to fast neutrons to determine the Si content, thermal neutrons for the Al content, and slow neutrons for longer periods to determine the Na content. The degree of accuracy was found to be within ±1·75% for SiO_2, ±0·9% for Al_2O_3, and ±0·3% for Na_2O.
                              CHEM. ABSTR.

4269. Micro-determination of water by titration with Fischer reagent. E. L. Bastin, H. Siegel and A. B. Bullock (General Electric Co., Emeryville, Calif., U.S.A.). *Anal. Chem.,* 1959, **31** (3), 467–473.—Details of a special apparatus and of its use are given for the determination of quantities of H_2O in the range 0·01 to 3 mg.
                      H. F. W. KIRKPATRICK

4270. Non-dispersive infra-red analysis of mixtures of water and heavy water. C. A. Bosselaar (Stichting voor Fundamenteel Onderzoek der Materie, Utrecht). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/2250, 7 pp.—The deuterium content can be determined by means of a non-dispersive i.r. gas analyser. An apparatus is described to measure the D_2O content of vapour mixtures from the natural concn. range to 40% of D_2O with an accuracy of about 0·5% of D_2O. Much better results can be obtained with liquid mixtures. The method is suitable for rapid determinations on flowing streams of water.
                              NUCL. SCI. ABSTR.

4271. Determination of lithium in lithium-magnesium alloys. D. H. Wilkins (General Electric Co., New York, U.S.A.). *Anal. Chim. Acta,* 1959, **20** (2), 116–118.—*Procedure*—Dissolve a 0·5-g sample in dil. HCl, evaporate to dryness and dissolve the residue in water with sufficient dil. HCl to produce a clear soln. Dilute to 100 ml and transfer 10 ml to a column (1 cm × 50 cm) of strongly acidic cation-exchange resin (H+ form, 100 to 150 mesh), washing the soln. into the resin with water. Elute the Li+ with 150 ml of 0·5 N HCl. Evaporate the eluate to dryness, dry the residue at 110°, dissolve it in water and titrate with standard $AgNO_3$ soln. To regenerate the column, elute the Mg^{2+} with 4 N HCl.   H. N. S.

4272. Complexometric determination of sodium. A. Holasek and M. Dugandžić (Univ., Graz, Austria). *Mikrochim. Acta,* 1959, (3), 488–489.—In the titration of Zn contained in the ppt. of sodium zinc uranyl acetate, dithizone is used as indicator in place of Eriochrome black T. Even when using 0·001 M EDTA, a sharper change is observed. Very good recovery is shown within the range from 80 to 318 μg of added Na.   D. F. PHILLIPS

4273. Determination of sodium from the zinc content of the triple uranyl acetate compound by extraction titration. L. V. Markova and K. E. Kleiner (Inst. of Gen. and Inorg. Chem., Acad. Sci., UkrSSR). *Zavod. Lab.,* 1959, **25** (2), 144–145.—The sodium zinc uranyl acetate compound is pptd., washed and dissolved, and the Zn content of the soln. is determined by dithizone extraction titration (Sandell, *Ind. Eng. Chem., Anal. Ed.,* 1937, **9**, 464). The determination of Na from the Zn content is satisfactory in the presence of 50 times as much K as Na.   G. S. SMITH

4274. Separation and determination of traces of sodium present in potassium salts. J. Angot (Soc. d'Études Chim. pour l'Ind. et l'Agric., Argenteuil, Seine-et-Oise, France). *Mikrochim. Acta,* 1959, (3), 346–356 (in French).—A preliminary separation of the trace amount of Na from K is carried out chromatographically on an ion-exchange column of Amberlite IR-120 (H+ form). The Na is eluted with 0·5 N HCl and the determination completed by flame photometry by using a very simple flame photometer in which the characteristic line is isolated by means of an interference filter. The excitation flame is fed by air - propane or air - butane. The absence of interfering ions facilitates the establishment of ideal conditions for the flame photometry. The determination of 0·05% of Na in potassium salts with a relative precision of $\simeq \pm 5\%$ has been achieved, but it is envisaged that, by the use of certain special precautions (*e.g.*, the use of quartz for the ion-exchange tube and its accessories, a laboratory with a dust-free atmosphere and rigorous purification of reagents), it should be possible to determine 0·001% of Na with a relative precision of ±10%.   D. F. PHILLIPS

4275. Determination of potassium and sodium in mixtures of their salts by means of cation exchangers. G. Gabrielson (Elektrokemiska AB, Bohus, Sweden). *Anal. Chim. Acta,* 1959, **20** (2), 146–151.—To determine NaCl and KCl in a soln. of the two salts a portion is first evaporated to dryness to find the total content. Then a similar portion is passed through a column of Amberlite IR-120, charged with K+, to exchange Na+ for K+, and the resulting soln. is evaporated to dryness and the NaCl is calculated from the gain in wt. over the original content. Alternatively, the KCl may be determined by exchanging K+ for Na+ and calculating from the loss in wt. In another less accurate procedure, both Na+ and K+ are exchanged for H+ and the resulting soln. is titrated with standard NaOH soln. This titre, and the total wt. of dry salts determined in a similar sample, provide the data for the calculation of the components.   H. N. S.

4276. Spectrophotometric micro-determination of potassium and sodium. F. Kreisky (Pharmakol. Inst., Univ., Gotenburg, Sweden). *Mikrochim. Acta,* 1959, (2), 243–248 (in German).—Potassium in tissues in the concn. range of 4 to 40 μg can be determined as potassium iodoplatinate and Na (3·2 to 32 μg) as sodium zinc uranyl acetate. *Procedure for potassium*—The sample (8 to 80 μg of KCl) in 0·01 N HCl is treated with 0·1 ml of 0·5% chloroplatinic acid in a calibrated 15-ml centrifuge

tube, placed in a water bath and evaporated to dryness at 90° to 95°. When cool, the residue is first moistened with 1 ml of abs. ethanol, then a further 10 ml is added and the mixture is centrifuged for 20 min. After decantation it is washed with ethanol (1×7 ml, 3×5 ml), being centrifuged each time for 12 to 15 min. Last traces of ethanol are removed at 90° to 95°, 6 ml of N HCl is added, and the soln. is transferred to a 10-ml flask and set aside overnight. To an aliquot containing 0·6 to 6 μg of KCl per ml is added 0·5 ml of KI soln. (5%), the mixture is made up to 5 ml with N HCl and set aside for 4 hr. in the dark. The extinction is measured at 496 mμ. A blank determination is carried out at the same time. *Procedure for sodium* —The sample (0·5 to 1 ml in 0·01 N HCl, containing 6 to 80 μg of NaCl per ml) is placed in a 15-ml calibrated centrifuge tube and evaporated in a water bath. When the residue is cool, 0·08 ml of tri-chloroacetic acid (2%) is added followed, in subdued light, by 1 ml of zinc uranyl acetate soln. (specified) and 0·5 ml of abs. ethanol. After being set aside overnight, the mixture is centrifuged for 30 min., then decanted, washed with acetone (2×5 ml) and centrifuged each time for 20 min. The acetone is evaporated at 90° to 95° for 12 min. and 6 ml of Na citrate soln. (0·4%) is added. The soln. is transferred to a 10-ml flask, washed with 4 ml of Na citrate soln. and made up to 10 ml with Na citrate soln. After 2·5 hr. the extinction is measured at 224 and 244 mμ. The accuracy is within $\pm$ 5·5% for K for 4 to 8 μg and $\pm$ 2% for 20 to 80 μg, and $\pm$ 1·5% for Na.　　　B. B. BAUMINGER

4277. Determination of alkali hydrogen carbonates in the presence of alkali carbonates. E. Bakács-Polgár and L. Szekeres (Inst. f. Chem. d. Tierärztl. Hochsch., Budapest). *Pharm. Zentralh.*, 1959, **98** (1), 3–5.—Add a known excess of NaOH soln. to the mixture (containing approx. equal amounts of HCO_3^- and CO_3^{2-}), shake vigorously with a slight excess of $BaCl_2$ soln., set aside for a few minutes and titrate with $ZnCl_2$ soln., with phenolphthalein as indicator (*cf. Anal. Abstr.*, 1958, **5**, 3265).
　　　A. R. ROGERS

4278. Analysis of soda ash (anhydrous sodium carbonate). Proposed revision of TAPPI standard T612m-44. *TAPPI*, 1958, **41**, 167A–168A.—In this revision, apparatus, reagent and report sections have been added and a weighing bottle substituted for a weighing tube for measuring the loss of weight at 150°. *Total alkalinity*—A 250-ml portion of the soln. (corresponding to 2·5 g of the specimen) is titrated quickly with 0·5 N HCl, with 3 drops of methyl orange as indicator. To another 250 ml about 1 ml less of 0·5 N HCl is added, CO_2 is removed by boiling and the titration completed after cooling. *Hydroxide*—To 250 ml of soln. is added 100 ml of 10% $BaCl_2$ soln. and the ppt. is filtered off. The filtrate is titrated with 0·5 N HCl to phenolphthalein. *Bicarbonate*—A 10-g portion of solid in 50 ml of H_2O is titrated with 0·5 N NaOH until one drop produces an immediate dark coloration with $AgNO_3$ soln. Bicarbonate cannot be present together with hydroxide. *Carbonate*—This component is calculated from the bicarbonate and total alkalinity values.
　　　R. AICHER

4279. Determination of free potassium metal in coloured potassium chloride. L. Silverman and M. E. Shideler (Atomics International Div., N. Amer. Aviation, Inc., Canoga Park, Calif.). *U.S. Atomic Energy Comm.*, Rep. NAA-SR-1421, 1956,

13 pp.—The free K reacts with water to form KOH, and the hydroxyl ion concn. is determined by pH change. A particularly useful pH range of 5 to 9 was selected. Coloured crystals were produced by the action of K vapour on halide crystals, and the experimental results of the analysis of the coloured KCl crystals are shown to be within the 95% confidence level.　　　NUCL. SCI. ABSTR.

4280. Determination of ammonium and potassium ions in mixtures of alkali metals. Use of mercury(II) - EDTA. F. S. Sadek and C. N. Reilley (Dept. of Chem., Univ. of N. Carolina, Chapel Hill). *Anal. Chem.*, 1959, **31** (4, Part I), 494–498.—*Procedure A (for NH_4^+ in the presence of Na and free NH_3)*—Pipette an excess of Hg^{II} - EDTA soln. [a stoicheiometric mixture of acidic $Hg(NO_3)_2$ and EDTA, 0·1 M soln., neutralised to pH 6·8] into a flask; add 6 drops of bromothymol blue (0·1% in methanol) and 3 drops of red dye (*e.g.*, 0·1% Ponceau PXO in H_2O) and adjust to pH 6·8 (grey colour). Add the sample soln., which gives a yellow colour, then titrate with 0·1 N NaOH back to grey. Sodium, K and free NH_3 in 100-fold excess do not interfere, SO_4^{2-} and small amounts of Cl^- or F^- can be tolerated, but PO_4^{3-} must be absent. When Ca, Mg, Cu and Fe are present, their EDTA titre must be found and allowed for. *Procedure B (for NH_4^+ and K^+)*—Neutralise the sample (containing $\not>$ 10 mg of NH_4^+ and K) with pure NaOH or HCl and dilute to 50 ml. Add conc. HCl (0·5 ml) and 10 ml of Na tetraphenylboron (**I**) soln. (3 g of **I** in 100 ml of H_2O, shaken with pure Al_2O_3 and filtered). Stir and filter after 5 min. through a No. 4 or 5 sintered funnel. Wash the ppt. with H_2O and dissolve it in 4 to 10 ml of dimethylformamide. Transfer the soln. to the original beaker, add an excess of Hg^{II} - EDTA soln., adjust to pH 4·5 to 6·0, stir and dilute to 200 ml. Neutralise with NaOH, add excess of aq. NH_3 buffer soln. (pH 10) and a few drops of 0·1% Eriochrome black T soln. Titrate from blue to red with standard Mg soln. The procedure can be applied to other insol. compounds of **I**.　　　P. D. PARR-RICHARD

4281. Rapid method for the determination of rubidium in silicate minerals. E. S. Burkser and T. G. Kornienko. *Ukr. Khim. Zhur.*, 1958, **24** (3), 375–378; *Ref. Zhur., Khim.*, 1959, (1), Abstr. No. 914.—The use of the radioactive isotope ^{86}Rb is proposed for establishing the losses of Rb, amounting to 20 to 50%, observed in the determination of Rb in silicate rocks by a gravimetric method. The use of ^{86}Rb simplifies the method and considerably shortens the time for the analysis (from 20 or 25 days to 10 days). To the sample of silicate rock add a known amount of ^{86}Rb and decompose the sample with HF. Treat the residue with $Ca(OH)_2$, and precipitate Ca from the resulting soln. of alkali-metal hydroxides as carbonate and oxalate. Remove ammonium salts and oxalic acid from the soln. of alkali-metal carbonates, and convert the carbonates into chlorides. To concentrate Rb, evaporate the soln. to dryness and extract the residue three times with a mixture of water (1 ml) and ethanol saturated with HCl (4 ml). To the separated mixture of salts add water (0·3 ml) and a mixture of ethanol and conc. HCl (2 : 1) (2·7 ml), and set aside for 10 to 12 hr. to separate KCl. Then precipitate Rb from the hot ethanolic soln. with a 40% ethanolic soln. of $SnCl_4$ and weigh the ppt. of Rb_2SnCl_6. Measure the β-activity of the ppt. and compare it with the activity of a standard containing the same amount of ^{86}Rb as was added

to the rock sample, and so calculate the content of Rb in the rock. The described method has been tested on the determination of Rb in biotites.

C. D. KOPKIN

4282. Increase of sensitivity and accuracy of the flame-photometric determination of caesium in minerals. E. A. Fabrikova (Inst. of Mineral., Geochem. and Crystallochem. of Rare Elements, Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (1), 41–44.—The presence of other alkali metals, when in greater concn. than Cs, increases the intensity of the line due to Cs at 8521 A; K has the greatest effect; as the concn. of K increases, the intensity reaches a max. which is up to 25 times higher than normal. The standard curve of intensity *vs.* concn. of Cs (0·2 to 100 μg per ml) in the presence of 2500 μg of K per ml is almost rectilinear. At the saturation intensities, the addition of Na, Li or Rb has an imperceptible influence on the emission of Cs. To determine Cs, moisten the sample (0·5 to 1 g) in a platinum dish, add conc. H_2SO_4 (0·4 ml), HF (20 ml) and HNO_3 (2 or 3 drops), heat to 70° or 80° to decompose the sample, increase the heating to fumes of SO_3, cool, add water (2 ml) and conc. H_2SO_4 (0·1 ml), again heat to fumes, evaporate again after adding water (5 ml), dilute with 25 or 30 ml of water and heat to dissolve. Dilute to 70 ml, heat just to boiling, add powdered basic lead carbonate with stirring till alkaline to methyl red, boil for several minutes, stir and filter. Wash the residue with hot water to give a total filtrate of 120 to 130 ml, evaporate to 30 ml, and cool; filter, and make the filtrate up to 50 ml. Determine K with the lines 7665 and 7699 A. To 20 ml of soln. add sufficient K_2SO_4 soln. (0·0557 g per ml) to give, after dilution, 2·5 mg of K per ml, dilute to 25 ml, and determine Cs at 8521 A. The mean relative error is ±4·45% for 0·01% and ±9·7% for 0·001% of Cs. The determinable minimum is 0·2 μg of Cs per ml.

C. D. KOPKIN

4283. Analytical use of pyridino-copper fumarate. A. I. Cherkesov, A. S. Mel'nikova and T. S. Zhigalkina. *Trudy Astrakhansk. Tekhn. Inst. Rybn. Prom. i Khoz.*, 1958, (5), 143–146; *Ref. Zhur., Khim.*, 1959, (3), Abstr. No. 7969.—The interaction of Cu^{2+} with a soln. of fumaric acid and pyridine (2·5 g of fumaric acid in 100 ml of aq. *M* pyridine) forms pyridino-copper fumarate, of the composition $[Cu(Py)_2]C_4H_2O_4.H_2O$ (I), which is insol. in water, ether, ethanol, $CHCl_3$ and other organic solvents. I dissolves in conc. aq. NH_3 to form the cuprammonium complex, and in HCl, H_2SO_4 and HNO_3 to form the corresponding salts. On being heated to 100°, I loses its water of crystallisation, and at higher temperatures decomposes with the formation of CuO. I may be used for the gravimetric determination of Cu (weighed as CuO) and for the microcrystalloscopic detection of Cu in the presence of the alkali and alkaline-earth metals, Ni (<10 mg per ml), Pd (<1 mg per ml), Cd, Co, Zn, Mn and Cr. For the detection, place 1 drop of test soln. on a slightly warm slide and add 1 drop of reagent soln.; in the presence of Cu, large blue crystals of I are deposited from the cooled soln.; these coalesce into ribbons. The detectable minimum of Cu is 0·2 μg; the limiting dilution is 1 in 5 × 10⁴. The presence of Bi, Fe and Al greatly lowers the sensitivity.

C. D. KOPKIN

4284. Rapid determination of copper and zinc in brass solutions. R. C. Armét. *Electroplating*, 1959, **12** (2), 56–57.—A rapid and accurate method consists in determining Cu by the iodine - thiosulphate procedure, followed by determination of Zn by EDTA, with Xylenol orange as indicator. Results of analyses of different brass soln. by this process and by the electrolytic method are tabulated and show satisfactory agreement.

C. H. COWPER-COLES

4285. Controlled-potential coulometric determination of copper and uranium. W. D. Shults and P. F. Thomason (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 492–494.—Solutions of mixed copper and uranium sulphates can be analysed with coeff. of variation of ≃ ± 0·1%, regardless of the Cu to U ratio. Two titrations are performed, the first, a reduction at −0·3 V in which both elements are reduced, and the second, a re-oxidation of the Cu alone at +0·175 V.

K. A. PROCTOR

4286. Spectrographic determination of copper, lithium and rubidium in mineral salts. B. O. Filonov and M. M. Pavlyuchenko. *Sb. Nauch. Rabot. Inst. Khim., Akad. Nauk BSSR*, 1958, (6), 92–101; *Ref. Zhur., Khim.*, 1959, (3), Abstr. No. 8014.—The analysis is made by the method of standard additions, the unknown concn. *x* being calculated from the formula $x = a^2(c - 2a)$, where *a* and *c* are the amounts added [Pavlyuchenko *et al.*, *Sb. Nauch. Rabot. Inst. Khim., Akad. Nauk BSSR*, 1958, (6), 102; *Ref. Zhur., Khim.*, 1959, Abstr. No. 986]. The sample is introduced into an a.c. arc discharge on a moving electrode. To determine Cu, a hole is made in a horizontal carbon electrode and is filled with the powdered sample. A sensitivity of 10⁻⁶ % is achieved by using the line Cu 3247·5 A with Ag 3286·7 A as comparison line. The samples are vaporised at 8 amp. For Li and Rb the analytical lines are Li 6707·8 A and Ba 6675·2 A, and Rb 7800·2 A and Ba 7911·35 A. The sensitivity is 5 × 10⁻⁵ % for Li and 5 × 10⁻⁴ % for Rb. The mean error of two determinations is ± 10 %. It is established that by diluting the samples of Cu and Li with NaCl and carbon powder, and by evaporating the substance completely from the electrode groove, the influence of third components is practically eliminated and a single graph may be used.

C. D. KOPKIN

4287. High-frequency titrations. I. The silver - thiocyanate reaction. Bharat R. Sant and Anil K. Mukherji (Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chim. Acta*, 1959, **20** (2), 124–127.—The high-frequency method is applied to the titration of Ag⁺ (3·2 to 6·7 mg), in concn. down to 0·0003 M, with KSCN. At the lowest concn. the error is ≃5%. Similar accuracy is obtained in the titration of KSCN or NH_4SCN with standard $AgNO_3$ soln.

H. N. S.

4288. High-frequency titrations of silver and thallium(I) with sodium tetraphenylboron. Anil K. Mukherji and Bharat R. Sant (Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 608–610.—The pptn. of Ag or Tlᴵ with Na tetraphenylboron (I) was studied by high-frequency titration, and the stoicheiometric formation of Ag tetraphenylboron or Tl tetraphenylboron was confirmed. The method is suitable for milligram amounts of Ag or Tl and for dilute soln. of tetraphenylboron ions, with an error of 1%. The concn. of the titrant was adjusted so that the total vol. change was ≯ 3%, and the end-point was found graphically. When Ag⁺ or Tl⁺ are titrated with I, the capacitance at first decreases

and then increases after the end-point. In reverse titrations, there is continuous increase in the readings, the slope of the curve being steeper after the end-point.   P. D. PARR-RICHARD

4289. Determination of gold in alloys with copper and silver by means of potentiometric titration with quinol. A. Czapliński and K. Trokowicz (Dept. of Tech. Analysis, Polytech. Inst., Gdansk). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 463–469.—When the alloy is dissolved in aqua regia, Au is converted into $AuCl_3$ which, in the presence of an excess of HCl, changes into $HAuCl_4$, producing with NaCl a stable salt, $NaAuCl_4$, which in turn is reduced by quinol to Au according to the equation—

$$2NaAuCl_4 + 3C_6H_4(OH)_2 = \\ 3C_6H_4O_2 + 2NaCl + 6HCl + 2Au.$$
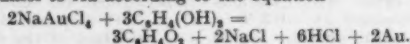
Under strictly controlled conditions this reaction can be applied to quant. determination. *Procedure*—The sample (140 mg of Au) is dissolved in aqua regia in the presence of NaCl, evaporated nearly to dryness, cooled, treated with 10 ml of conc. HCl and the volume reduced to 1 ml by evaporation. This soln. is diluted to 100 ml with H_2O, the AgCl ppt. is filtered off and the filtrate is made up to 250 ml with H_2O. An aliquot (25 ml) is again diluted to 100 ml and titrated with 0·01 N quinol at room temp., with a platinum and calomel electrode pair. The potential jump at the end-point exceeds 100 mV. It is suggested that this method can be applied to gold alloys containing Cu, Ag, Sn and Cd.   W. B. MIASKOWSKI

4290. New analytical methods for beryllium. Kenji Motojima (Atomic Energy Res. Inst., Japan). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/1325, 23 pp.—8-Hydroxyquin-aldine was found to be useful as an analytical reagent for the determination of beryllium. With this reagent, Be can be determined gravimetrically, volumetrically, spectrophotometrically and even fluorimetrically. One of the main advantages of these methods lies in the elimination of Al interference, which is common in the usual Be determinations. Consequently, no preliminary separation of Al is required and a simple and accurate analytical method for Be determination is thus provided.
                    NUCL. SCI. ABSTR.

4291. Fluorimetric determination of sub-microgram quantities of beryllium. C. W. Sill and C. P. Willis (Health and Safety Div., U.S. Atomic Energy Comm., Idaho Falls). *Anal. Chem.*, 1959, **31** (4, Part I), 598–608.—By the fluorimetric method described, $\not< 0·0004\ \mu g$ of Be can be detected with good precision. The permanent glass standards used (made from uranium glass spheres fused into borosilicate glass) show no decrease in fluorescence in low-intensity u.v. light. *Procedure*—To a sample of Be in 0·5 ml of $HClO_4$ add 8·2 N NaOH (3 ml) and 3 drops of 0·01% quinine sulphate in water containing 2% (v/v) of 72% $HClO_4$. Add $HClO_4$ sufficient to give a brilliant blue fluorescence under u.v. light; add 1 drop in excess, and transfer the soln. to a 25-ml flask. Add 0·5 ml of triethanol-amine (**I**) - EDTA (5 g of EDTA and 3 ml of **I** in 95 ml of H_2O), then sufficient N NaOH to extinguish the fluorescence and 2 drops in excess. Add 0·5 ml of sodium stannite (1·5 g of $SnCl_2.2H_2O$ in 25 ml of H_2O, poured into 2·4 g of NaOH in 10 ml of H_2O and diluted to 50 ml) and 5 ml of buffer soln. (50 ml of piperidine added to 10 g of hydrazine sulphate and 5 g of EDTA in H_2O, and diluted to 500 ml).

Mix and dilute to vol. Add 1 ml of morin soln. (25 ml of 8 M $NaClO_4$ and 2 drops of 10% EDTA soln. mixed with 7·8 mg of morin in 25 ml of ethanol and diluted with H_2O to 100 ml) under the surface of the soln. Mix and place in a bath controlled to within $\pm 2°$ of room temp., then measure the fluorescence, which is a linear function of the concn. of Be up to 1 μg per 26 ml. The effects of morin concn., alkalinity, the oxidation of morin, the hydrolysis of Be and the presence of other metals are discussed. Methods for preparing Be soln. suitable for the above procedure are described for urine, bone, ores, steel, air-dust and smear samples. Beryllium can be extracted with acetyl-acetone and $CHCl_3$; heavy metals are complexed with EDTA.   P. D. PARR-RICHARD

4292. Rapid determination of beryllium in beryl mineral. J. L. Huguet and C. L. Bamberger (Comisión Nacional de Energía Atómica, Buenos Aires). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/1578, 7 pp.—A study was made of the attack of mineral beryl with Na_2CO_3 and of the determination of Be by the direct pptn. produced by the attack, in which no previous separation (including that of SiO_2) has been made. The conclusion is reached that, provided that some precautions are observed, the technique remains applicable, markedly reducing the time usually taken by the conventional method.
                    NUCL. SCI. ABSTR.

4293. Determination of the oxygen content of beryllium metal by activation. R. F. Coleman and J. L. Perkin (U.K.A.E.A., Atomic Weapons Res. Estab., Aldermaston, Berks., England). *Analyst*, 1959, **84**, 233–236.—The beryllium sample was irradiated in a 14·5-MeV neutron flux and the residual activity was measured with a Geiger counter. The 7·4-sec. β-activity from ^{16}N produced in the reaction $^{16}O(n,p)^{16}N$ was then compared with the activity from a similar-sized sample containing a known amount of O. The neutron flux was obtained by bombarding a tritiated zirconium target with 500-keV deuterons, the output being maintained at $\simeq 10^{10}$ neutrons per sec. with an exposure of the sample of 1 to 10 sec. For the calibration of the standard beryllium, known mixtures of beryllium and its oxide were prepared in an atmosphere of argon. These were compacted and sintered *in vacuo* and machined to a standard size, corrections for variation in neutron dose, counter geometry and self-absorption of β-particles being thus avoided. The added O in the five samples used ranged in equal increments from nil to 1·60%. Each was irradiated and counted as described. The method had satisfactory precision with amounts of O down to 0·001%. Five impurities with half-lives of 5 to 15 sec. could occur in beryllium, *viz*, S, Si, Al, Mg and F. The max. limits for these are given. As little as 0·005% of O can be measured with an error of $\pm$ 20%.   A. O. JONES

4294. Azo-dye derivatives of chromotropic and salicylic acids as reagents for magnesium. I. M. Korenman and E. I. Levina. *Uch. Zap. Gor'kovsk. Univ.*, 1958, (32), 149–160; *Ref. Zhur., Khim.*, 1959, (1), Abstr. No. 919.—The reactions of a large number of derivatives of chromotropic and salicylic acids with the alkaline-earth elements and Li in alkaline and ammoniacal media are studied. Most of the salicylic acid derivatives do not give characteristic colour reactions with these cations. The dyes

are the azo derivatives of chromotropic acid with $-C_6H_4NO_2$ (**I**) and $-(C_6H_4)_3 \cdot N : N \cdot C_6H_2(OH)_3(SO_3H)_3$ (**II**), which can be used to detect 0·5 to 1·0 μg of Mg at a limiting dilution of 1 in 2×10^6 in the presence of 300-fold amounts of alkaline-earth cations. To 1 ml of soln. add 1 or 2 drops of a soln. of the appropriate reagent and 3 or 4 drops of N NaOH or 4 N aq. NH_3, mix and warm to between 30° and 40° on a water bath. In the presence of Mg the colour of **I** changes from pink to blue or (in aq. NH_3) dark lilac, and the colour of **II** from pink (pink - lilac in aq. NH_3) to blue. **I** and **II** are the most sensitive reagents for Mg yet known.

C. D. KOPKIN

4295. Determination of magnesium in slags and scoriae by flame spectrophotometry. J. Coulombeau and M. Maire (I.R.S.I.D., Saint-Germain-en-Laye, France). *Chim. Anal.*, 1959, **41** (1), 3–11.—Conditions are defined for the spectrophotometry of the magnesium line at 2852·1 A. The method requires the removal of SiO_2 but not of other oxides. The sample soln. (*A*) is prepared by dissolving 2 g with HCl, evaporating twice to dryness with HCl to render SiO_2 insoluble, taking up with HCl and filtering. The residue is evaporated with HF to remove SiO_2, fused with $NaKCO_3$ or $KHSO_4$, taken up with HCl, added to the original filtrate, and the whole made up to 500 ml. Working soln. are prepared as follows. For Thomas slag containing 2 to 6% of Mg, take 10 ml of *A*, and make-up to 100 ml with a soln. (*B*) containing 60 ml of conc. $HClO_4$ and 34 ml of conc. HCl per litre. For Thomas slag containing 0·3 to 2% of Mg, take 10 ml of *A*, 10 ml of a soln. (*C*) containing 0·418 g of $MgCl_2.2H_2O$ per litre, and make up to 100 ml with *B*. For substances other than Thomas slag, take 10 ml of *A*, 10 ml of a soln. (*D*) containing 1 ml of conc. H_3PO_4 and 3·68 g of $CaCl_2.2H_2O$ per litre, and make up to 100 ml with *B*. For substances containing little Mg, take 10 ml each of *A*, *D* and *C*, and make up to 100 ml with *B*. The manipulation of the Beckman DU spectrophotometer (equipped for flame) is described. The difference between the peaks at 2843 and 2849 to 2852 A is measured, six soln. and two standards being used in a specified manner, and the result obtained by linear interpolation; MgO (%) = $n \times d \times 0·0415$, where n is the observed result in p.p.m. and d is the dilution. The actual measurement of six soln. occupies 1 hr., and the claimed accuracy is within $\pm 0·2\%$ of the absolute value.

R. E. ESSERY

4296. Simple spectrophotometric method for determining magnesium, calcium, strontium, barium, cadmium and zinc with ethylenediaminetetra-acetic acid. J. R. Dunstone and E. Payne (Biochem. Dept., Univ. of Queensland, Brisbane, Australia). *Analyst*, 1959, **84**, 110–113.—To construct the calibration graph, soln. containing 1·0 to 5·0 μmoles of metal ion are added to 1 ml of 0·005 M EDTA (disodium salt) and 1 ml of a buffer soln. (NH_4Cl - aq. NH_3, pH 10). Each mixture is diluted to 5 ml and its extinction at 225 mμ is measured against a blank soln. of 1 ml of buffer soln. diluted to 5 ml. The differences between the extinctions of these soln. and that of a mixture of 1 ml of EDTA soln., 1 ml of buffer soln. and 3 ml of water are plotted against the concn. of metal ion. A 1-ml aliquot of the sample soln. containing 1 to 5 μmoles of the metal ion is treated in the same way, and the extinction difference is referred to the calibration graph. The method is useful when an accuracy within $\pm 3\%$ is acceptable. In addition to the metal ion being determined, soln. for analysis

may contain only the alkali-metal ions (except Li) and NH_4^+. The method fails if anions absorbing strongly at 225 mμ (*e.g.*, NO_3^- and acetate) are present, but PO_4^{3-} in concn. 40 times that of the metal ion can be tolerated in the determination of Ca.

A. O. JONES

4297. Micro-determination of calcium. A. B. Gilbert (King's College, Univ. of Durham, Newcastle upon Tyne, England). *Nature*, 1959, **183**, 888.—Concentrations of Ca of $\simeq 10^{-2}$ μg have been determined in vol. of $\simeq 40$ μl of soln. with an accuracy of 1%, by using as indicator Na 1-(1-hydroxy-2-naphthylazo) - 5 - nitro - 2 - naphthol - 4 - sulphonate which is as suitable as but cheaper than Calcon (C.I. Mordant Black 17). The method is essentially similar to that of Hildebrand and Reilley (*Anal. Chem.*, 1957, **29**, 258).

K. A. PROCTOR

4298. Improved end-point by addition of poly-(vinyl alcohol) in the EDTA titration of calcium with Calcon as indicator. P. F. Lott and K. L. Cheng (Dept. of Chem. Engng, School of Mines and Metall., Univ. of Missouri, Rolla, U.S.A.). *Chemist Analyst*, 1959, **48** (1), 13.—The earlier procedure (*cf. Anal. Abstr.*, 1957, **4**, 3576) for the stepwise determination of Ca and Mg with EDTA has been improved by the substitution of poly(vinyl alcohol) (**I**) for gelatin to inhibit the adsorption of Calcon on the pptd. $Mg(OH)_2$ in the first stage. A soln. of **I** is prepared by mixing 2 g of a medium-viscosity **I** with 200 ml of boiling water in a homogeniser. The soln. keeps indefinitely. To the test soln. (up to 0·5 millimole of Ca plus Mg) add 2 or 3 drops of the soln. of **I**, adjust the pH to >12·5 with NaOH, add 3 drops of 10% KCN soln. and 3 drops of Calcon (C.I. Mordant Black 17) indicator soln. and titrate with 0·01 M EDTA to a red to blue end-point. (Soln. high in Mg should be warmed to 60° before adding the indicator, and titrated hot.) Then bring the pH to 10 with ammoniacal buffer, boil to dissolve $Mg(OH)_2$, add 1 ml of buffer and 1 drop of Eriochrome black T soln. and titrate hot to a red to blue end-point with EDTA soln. Heavy-metal interference is dealt with as in the original method.

R. E. ESSERY

4299. Partition of metal - 8-hydroxyquinoline compounds between water and organic solvents. IV. Investigation of the separation of calcium oxinate complexes and their photometric determination in chloroform solution. F. Umland and K.-U. Meckenstock (Inst. f. Anorg. Chem., Tech. Hochschule, Hanover, Germany). *Z. anal. Chem.*, 1959, **165** (3), 161–179.—Calcium forms several complexes with 8-hydroxyquinoline (**I**). The normal Ca - I_2 complex is extracted at pH 11·3 with $CHCl_3$ soln. containing > 7% of **I**, but if the $CHCl_3$ soln. of **I** contains 2% of n-butylamine, Ca is extracted quant. at pH 11 to 12 as $C_6H_6NH_3[Ca - I_3]$ which is used for the photometric determination of Ca by measuring the extinction of the organic layer at 370 to 380 mμ. The average error is $\pm$ 2% for 0·8 to 9·6 μg of Ca per ml and $\pm 10\%$ for 0·16 to 0·64 μg of Ca per ml. Interfering cations are either complexed with KCN or removed by a pre-extraction without the addition of butylamine. Detailed procedures are given and the practical application of the method is demonstrated.

B. B. BAUMINGER

4300. Rapid determination of calcium oxide in flux agglomerate, limestone, dolomite, and blast-furnace and open-hearth slag, in the presence of triethanolamine as complexing agent. V. D.

Konkin. *Byull. Nauch.-Tekhn. Inform. Ukr. Nauch.-Issled, Inst. Metall.*, 1958, (6), 111–115; *Ref. Zhur.,Khim.*, 1959, (3), Abstr. No. 7978.—To remove the interference due to Al, Cr, Mn and Mg in the complexometric determination of CaO, these metals are masked by means of triethanolamine (**I**), which form complexes with them that are more stable than those with EDTA (disodium salt) (**II**). *Procedure*—Dissolve 0·1 g of finely ground agglomerate by warming with 7 ml of conc. HCl, cool, add water (90 ml), indigo carmine soln. (0·25 g in 100 ml of 50% ethanol) (5 drops) and **I** (1·5 ml). Shake vigorously for about 30 sec., add 12 ml of 20% NaOH soln. and 0·15 g of a mixture of murexide and NaCl (1:100), mix well and titrate with a soln. of **II** ($\simeq$0·5%). Determine the concn. of the **II** soln. with a soln. of CaO and with a standard flux agglomerate. For difficultly soluble agglomerates, mix the sample with an equal amount of Na_2CO_3, heat for 2 min. at 850° or 900°, cool the sintered mass, dissolve it in HCl and continue as described above. To determine CaO in blast-furnace and open-hearth slags, first shake the sample (0·1 g) vigorously with 60 ml of boiling water, immediately add 20 ml of conc. HCl and continue shaking for a further 1 or 2 min. to dissolve Ca completely. The presence of $\not>$ 80 mg of Fe, 20 mg of Al, 8 mg of Mn, 20 mg of Mg and 4 mg of Cr does not cause interference. The determination of CaO in agglomerates takes about 15 min., and in limestone and slags 8 to 10 min.　　　C. D. KOPKIN

4301. Determination of zinc in aluminium and copper alloys. M. Freegarde (Bragg Lab., Naval Ordnance Inspection Dept., Sheffield, England). *Metallurgia, Manchr*, 1958, **58**, 261–262.—Zinc (and some Cu) is adsorbed from 0·12 N HCl, containing 10% of NaCl, on the strongly basic anion-exchange resin De-Acidite FF. Copper is eluted with 2 N HCl and Zn is then eluted with N HNO_3 and titrated with EDTA. Magnesium, Fe, Mn, Ni, Ti and Si do not interfere, but Sn must be removed. The method is satisfactory for the determination of Zn in the range 0·1 to 6% in alloys of copper and aluminium, and its accuracy is equal to that of classical methods.

J. W. O. PYEMONT

4302. Simple apparatus for the determination of mercury by amalgamation with gold. J. Lacy (African Explosives & Chem. Industries Ltd., P.O. Northrand, Transvaal). *Anal. Chim. Acta*, 1959, **20** (2), 195–197.—The apparatus is intended particularly for the determination of Hg in charcoal activated with $HgCl_2$. It consists of a 15-ml silica flask surmounted by a silica column that contains 5 to 6 g of crumpled gold foil $\simeq$0·0025 cm thick. A sample (1 g), containing $\not>$70 mg of Hg, is mixed in the flask with 1 g of fine iron powder and the mixture is covered with a 0·3-cm layer of ZnO. The weighed column is inserted in the neck of the flask, which is then heated with a low flame for 10 min. and at a dull red heat for 20 min., the column being protected with a shield from the heat of the burner. After cooling, the column is rinsed with acetone, dried and weighed. The column is regenerated by heating in a bunsen flame while air is passed through it to remove the Hg.

H. N. S.

4303. Solubility and amphoteric properties of mercuric oxide. T. M. Salem (Chem. Dept., Univ. Coll. for Girls, Ain Shams Univ., Heliopolis, Cairo, Egypt). *J. Indian Chem. Soc.*, 1959, **36** (2), 83–86.

—Mercury is determined potentiometrically with an error of $\not>$ 1% for concn. as low as 0·5 mg per 100 ml. Both $HgNO_3$ and $Hg(NO_3)_2$ soln. are titrated with standard KI soln.; an amalgamated platinum electrode (1 sq. cm) acts as indicator electrode and is connected to a calomel reference electrode by a KNO_3 - agar bridge. The method is applied to the determination of the solubility of HgO in water and in soln. of various pH values. At 35°, the solubility is $3·47 \times 10^{-4}$ moles of Hg per litre, and the iso-electric point occurs between pH 7·5 and 8·0.　　　J. H. WATON

4304. Spectrographic determination of boron in aluminium. B. Weszprémy and T. Török (Cspel Iron and Metal Works, Budapest). *Acta Chim. Acad. Sci. Hung.*, 1959, **19** (4), 357–361 (in German). —The method is applicable to concn. of B used in aluminium alloys, namely 0·01 to 0·5%. Standards for use in the routine procedure were prepared from boron and aluminium of 99·99% purity and analysed by spark spectroscopy in soln., the line pair B 2497·72 - Al 2567·98 being used. The routine analysis is carried out by a low-voltage technique with solid electrodes. The line pair B 2497·72 - Al 2459·82 is used. The interfering effect of Fe is corrected from an intensity measurement of the line Fe 2486·35. The coeff. of variation of 12 determinations was $\pm$ 5·7%.　　G. BURGER

4305. Accurate determination of microgram amounts of boron in aluminium and aluminium - uranium alloys by the methyl borate - curcumin - oxalic acid method. I. H. Crocker (Atomic Energy of Canada Ltd., Chalk River, Ontario). *Atomic Energy of Canada Ltd.*, Rep. CRDC–811, 1958, 26 pp.—The method is suitable for B concn. of 30 p.p.m. or higher. Boron is separated by distillation as methyl borate from a HCl soln. of the alloy and is determined spectrophotometrically by the boric acid - curcumin - oxalic acid colour reaction. A precision of $\pm$2% is attainable when the determination is performed with the utmost care. The accuracy is such that no bias need be given when a calibration curve is used.　　NUCL. SCI. ABSTR.

4306. Determination of boric acid in glass by distillation of methyl borate with circulation of methanol. P. Ehrlich and T. Keil (Anorg. Abt., Chem. Inst., Univ., Giessen, Germany). *Z. anal. Chem.*, 1959, **165** (3), 188–193.—The principle of the circulation system, which has been used by Pietzke and Ehrlich (*Angew. Chem.*, 1953, **65**, 131) for the determination of fluorine, has been adopted for the distillation of methyl borate. The apparatus is illustrated and the procedure for the distillation described. The distillate passes to a quartz flask, from which the methanol is boiled off and returns to the reaction flask. The alkaline soln. is neutralised with HCl, with an indicator of pH 4·4 to 5·6. In the volumetric determination, mannitol is added and the boric acid is titrated using α-naphtholphthalein as indicator. Smaller amounts of boric acid are determined colorimetrically by the method of Hatcher and Wilcox (*cf. Brit. Abstr. C*, 1950, 437), which is based on the reaction of B with a soln. of carmine in conc. H_2SO_4. The average error in the volumetric method is <3% for 1 to 10 mg of B and in the photometric method <10% for 1 to 20 μg of B. The practical application of the method is demonstrated by the determination of B in prepared mixtures of borax and silica and in technical glass samples.　　B. B. BAUMINGER

4307. Qualitative testing for borates by poly(vinyl alcohol). A. J. Monte-Bovi, J. J. Sciarra and C. Martorana (St. John's Univ., Coll. of Pharm., Jamaica, N.Y., U.S.A.). *Drug Standards*, 1959, **27** (1), 15–17.—The blue colour given by borates with poly(vinyl alcohol) and iodine is a more sensitive test than the colour with turmeric paper or the green flame produced on ignition with methanol and H_2SO_4. A borate - iodine reagent is suggested for the detection of poly(vinyl alcohol).

A. R. ROGERS

4308. Polarographic determination of aluminium. V. D. Bezuglyĭ (Kharkov Dental Materials Works). *Zavod. Lab.*, 1959, **25** (3), 277–280.—The method is based on the use of Ca gluconate (*cf.* Pecsok *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 202, 1489). With a basal soln. containing 5% of Ca gluconate and **3** to 5% of $CaCl_2$, $E_{\frac{1}{2}}$ for Al is -1.57 to -1.60 V *vs.* the S.C.E.; the wave is well defined and the relation between wave height and concn. is linear.

G. S. SMITH

4309. Solvent extraction of aluminium oxinate. Tomihito Kambara and Hiroshi Hashitani (Dept. of Chem., Ritsumeikan Univ., Kyoto, Japan). *Anal. Chem.*, 1959, **31** (4, Part 1), 567–569.—A theory for the extraction of Al oxinate by organic solvents is developed, and confirmed experimentally. Oxine (8-hydroxyquinoline) (**I**) exhibits amphoteric properties, and its distribution as cationic, anionic and mol. species in $CHCl_3$ or in H_2O is deduced; an expression is also given for the extractability of Al oxinate. The method of "logarithmic plot" used in the analysis of polarographic current - voltage curves is applied to find pH values corresponding to half-extraction or half-dissociation. The pptn. of $Al(OH)_3$ from neutral soln. can be avoided by adding **I** to the soln. before pH adjustment, followed by extraction with $CHCl_3$.

P. D. PARR-RICHARD

4310. Determination of aluminium in the rare earths. Yu. A. Chernikhov and B. M. Dobkina (State Sci. Res. Inst. of Rare Metals). *Zavod. Lab.*, 1959, **25** (2), 131–132.—Extraction of the soln. of the rare earths at pH 5 with $CHCl_3$ containing oxine separates Al which is then determined colorimetrically in the extract. With neodymium - magnesium alloys the sample (0·1 g) is attacked first in the cold and then by gentle heating with 3 ml of conc. HCl. With chloride melts obtained in the treatment of loparite ores the sample (0·1 g) is dissolved in water containing 0·5 ml of conc. HCl. In either case the soln. is evaporated nearly to dryness and the residue is dissolved by heating in 10 to 12 ml of water containing three drops of acetic acid. The soln. in a separating-funnel is treated with 0·1 g of hydroxyammonium chloride (to retain Ce in the Ce^{3+} form) and several ml of an acetate buffer soln. to pH $\simeq 4.5$, and then with 3 to 4 ml of $CHCl_3$ and 0·5 ml of 3% Na diethyl-dithiocarbamate soln., and shaken. The separated aq. layer is again extracted with $CHCl_3$ with the addition of 0·2 ml of the thiocarbamate soln., and the $CHCl_3$ soln. containing Cu, Fe and Ni are rejected. If a further extraction gives a coloured soln. the extraction is repeated. The aq. soln. is mixed with 2 ml of 2 M Na acetate (the pH should now be $\simeq 5$) and, if Th is present, with 4 to 5 ml of 0·2 M K H phthalate, and then shaken with a 0·5% soln. of oxine in $CHCl_3$ (once with 2 ml and once with 1 ml). The Al in the extract is determined visually by comparison with standards or by colori-

metric titration, or photometrically at 380 to 400 mμ. The method is sensitive to 0·01% of Al.

G. S. SMITH

4311. Potentiometric determination of aluminium in nickel-based heat-resisting alloys. A. A. Gorelova and L. Ya. Polyak. *Zavod. Lab.*, 1959, **25** (3), 285–287.—The determination of Al by titration with NaF soln. can be carried out either at pH 6 in the presence of a large amount of NaCl (whereby difficultly soluble cryolite is formed) or at pH 3·5 to 4·5 (whereby soluble, practically undissociated, AlF_3 is formed). To determine Al in alloys of Ni, Cr, Fe, Mo, W and Ti, the sample (0·25 g) containing 3 to 6% of Al is dissolved in 30 ml of aqua regia, and the soln. is evaporated to dryness, followed by treatment with 15 ml of dil. HCl (1:1) and re-evaporation. The residue is dissolved in 15 ml of dil. HCl (1:1) and 35 ml of water, and Cu, As, Sn and Sb are pptd. whilst Fe, Ti and Mo are reduced by treatment of the soln. with granulated zinc. After 5 min. the remaining zinc is filtered off and washed with 1% HCl soln. (3 × 10 ml) and then with water, and the filtrate and washings are neutralised with aq. NH_3 and dil. HCl. For the cryolite method, the soln. (100 ml) is treated with 3 ml of dil. HCl (1:1), 10 g of NaCl and 25 ml of 50% Na acetate soln. to give a pH of 6, and then titrated with 0·25 N NaF to the first sharp potential jump. The indicator electrode is of aluminium and the reference electrode of nichrome, spaced 5 cm apart and immersed to a depth of 1 to 2 cm. For the AlF_3 method, the soln. (100 ml) is treated with 3 ml of dil. HCl (1:1) and 10 ml of 50% Na acetate soln. to give a pH of 3·5, and titrated. The methods are equally accurate.

G. S. SMITH

4312. Photometric determination of small amounts of phosphorus in aluminium alloys. Z. Večeřa and B. Bieber (State Res. Inst. of Materials and Technol., Brno, Czechoslovakia). *Hutn. Listy*, 1959, **14** (1), 56–58.—*Procedure*—To the sample (1 g) in a distillation flask add H_2O (5 ml), remove air by bubbling for 10 min. with CO_2, add HCl (1:1) (25 ml) and distil the PH_3 into a vessel containing Br, with occasional addition of HCl. Remove the excess of Br by heating, add a small amount of Na_2SO_3, boil for 3 min., transfer to a 100-ml separating-funnel, dilute with H_2O to 40 ml, add N H_2SO_4 (2 ml), ammonium molybdate soln. (100 ml of 5% ammonium molybdate soln. mixed with 100 ml of 10 N H_2SO_4) (5 ml) and extract with 40 to 50 ml of butanol. Wash the butanol layer with 0·5 N H_2SO_4 (2 × 40 ml), transfer it to another separating-funnel containing 40 ml of N H_2SO_4 and $SnCl_2$ soln. (0·5 ml), shake for 2 to 3 min., separate the aq. layer, dilute the blue butanol layer to 100 ml with butanol and measure the extinction at 720 mμ after 20 min. Compare with a calibration curve. Silicon hydride and H_2S do not interfere. Interference by As can be avoided by the addition of H_2SO_3 or thiourea. The method requires $\geqslant 1.5$ to 2 hr. and has been tested with good results by the analysis of silumin samples containing 10% of Si, 0·2 to 0·4% of Mn, 0·2% of Fe and 0·3% of Mg.

J. ZÝKA

4313. Photometric determination of gallium using Malachite green. J. Jankovský (Inst. for Ore Res., Prague). *Talanta*, 1959, **2** (1), 29–37.—Malachite green (C.I. Basic Green 4) forms a blue-green benzene-soluble complex with Ga in conc. HCl soln. *Procedure*—Transfer a 5-ml aliquot containing up to 5 μg of Ga in HCl (1:1) to a dry

25-ml flask, add conc. HCl (1 ml), TiCl₃ soln. (15%) (0·5 ml) and mix. After 5 min. add Malachite green soln. [2% in HCl (1:3)] (2 ml). Mix, add 5 ml of benzene and shake for 2 min. Measure the extinction of the benzene layer at 660 mμ in a 1-cm cell. The method is suitable for the determination of 0·001% of Ga in bauxite, zinc ores and ashes; smaller quantities can be determined after a concentration step comprising extraction with di*iso*propyl ether. The interfering effects of 64 foreign ions are tabulated. W. T. CARTER

4314. Photometric determination of traces of gallium with stilbazo as reagent. I. M. Z. Yampol'skiǐ. *Ich. Zap. Kursk. Gos. Ped. Inst.*, 1958, (7), 67–72; *Ref. Zhur., Khim.*, 1959, (2), Abstr. No. 4306. —Stilbazo forms with Ga³⁺ a red - violet compound. The intensity of the colour is proportional to the concn. of Ga up to 7 μg in 3 ml of soln., and increases with increase of pH, the optimum pH being 6·1 to 6·5. For the photometric determination of Ga, to 2 ml of ammoniacal acetate buffer soln. (pH 6·5) add the test soln. and 0·5 ml of a 0·001% soln. of stilbazo (total vol. 3·0 ml), and measure the extinction of the resulting soln. in a 5-mm cell at 530 mμ, with water as comparison soln. At pH 4·0 no interference is caused in the determination of <5 μg of Ga by the presence of >400 μg of Cd, >300 μg of Zn, and >200 μg of Al. The method may be used for the determination of Ga in metallic zinc; dissolve 1 g of technical zinc in 20 ml of HCl and, after electrolytic removal of Cu and Pb, determine Ga in the soln. by the method of additions (add 8 μg of Ga to 0·5 g of Zn). One determination takes 2 to 3 hr. C. D. KOPKIN

4315. Investigation of the extractive separation of gallium and indium with different solvents. H. Hartkamp and H. Specker (Inst. f. Spectrochem., Dortmund-Aplerbeck, Germany). *Talanta*, 1959, **2** (1), 67–72 (in German).—The procedure previously described (*Anal. Abstr.*, 1957, **4**, 1160) has been further studied. It is concluded that the In is best extracted with *cyclo*hexanone from a 0·2 N H₂SO₄ soln. containing a 6 to 10-fold excess of KI. Chloride and bromide must be absent. By the same procedure, In can also be quant. separated from Fe, Al and the alkaline-earth metals.
W. T. CARTER

4316. New fluorimetric method for determining indium. I. A. Blyum and T. K. Dushina (Central Ores Lab., Chelyabinsk Geological Trust). *Zavod. Lab.*, 1959, **25**, 137–139.—The method is based on the fluorescence excited by u.v. irradiation of benzene soln. of the complex formed b In andy Rhodamine 3B (C.I. Basic Violet 11) in the presence of HBr. By extracting 10 ml of a soln. of In, 2·5 M in HBr, mixed with 0·1 ml of 0·25% Rhodamine 3B soln., with 5 ml of benzene, and irradiating the extract, 0·02 μg of In can be detected. No interference is caused by K, Na, Mg, Ca, Cd, Al, Ga, Sn²⁺, Sn⁴⁺, Ti⁴⁺, Ge, Sb³⁺, Bi, V⁴⁺, Cr³⁺, Tl⁺, W, Pt, Mo, Co, Ni, Fe²⁺, Mn²⁺, Cu²⁺, SO₄²⁻ and PO₄³⁻, but fluorescence occurs with Au³⁺, Tl³⁺, Hg²⁺, Sb⁵⁺, Cu⁺, Pb, V⁵⁺, Cr⁶⁺, Se⁴⁺, Te⁴⁺, As⁵⁺, Fe³⁺, Zn, Ag and NO₃⁻. The reagent is most sensitive to In; thus the same fluorescence intensity is given by 1 μg of In as by 5 μg of Au, 4 μg of Tl, 5 μg of Te, 8 μg of Hg, 20 μg of Ag, 40 μg of Cr₂O₃²⁻, 2000 μg of Pb or 6000 μg of Zn. By preliminary reduction with iron, the interference of Au, Ag, Tl, As, Se, Te, Fe, Cr, Sb and V can be prevented. For general use in determining In, a

preliminary extraction of InBr₃ with butyl acetate is recommended. To determine In in ores of Cu and Zn, etc., the sample (0·1 g) is dissolved by treatment in the cold with 10 ml of conc. HNO₃, and 5 ml of conc. HCl followed by gentle heating for 2 to 3 hr. The soln. is evaporated nearly to dryness and the residue is mixed with 3 to 4 ml of conc. HBr and the soln. is again evaporated, the treatment with HBr and evaporation being repeated. The dry residue is dissolved in 10 ml of 5 N HBr and the In is extracted with 10 ml of butyl acetate. The extract is washed with 5 N HBr (2 × 2 to 3 ml) and the In is re-extracted with dil. HCl (2:1) (2 × 10 ml). After the addition of 1 mg of FeCl₃ or Fe₂(SO₄)₃ (as a collector) and 5 ml of dil. H₂SO₄ (1:1) and 1 ml of H₂O₂ soln. (to destroy organic matter) the soln. is evaporated to fuming, a further amount of H₂O₂ being added if the residue chars. The residue is diluted to between 30 and 40 ml and treated with an excess of aq. NH₃. The collected and washed ppt. is dissolved in 2·5 N HBr and the soln. is treated with 0·02 to 0·03 g of iron (reduced with H) and set aside for 2 hr. The filtered soln. is treated with two drops of a 0·10 soln. of Rhodamine 3B in water and the complex is extracted with 5 ml of benzene. The fluorescence of the extract is compared with that of standards. G. S. SMITH

4317. Co-precipitation of thallium with zinc sulphide. G. V. Efremov and S. A. Leont'eva. *Vestn. Leningr. Univ.*, 1959, No. 4, *Ser. Fiz. i Khim.*, (1), 141–144.—The conditions for quant. co-pptn. as regards the relative proportions of Tl and Zn, the pH of the soln. in which the pptn. takes place, the dilution of the soln. and times required for pptn. are specified. The data obtained indicate that this co-pptn. can be used for the analysis of zinc metal, zinc ores and zinc waste, and for the micro-determination of Tl. K. R. C.

4318. Photometric determination of total rare-earth elements in ores and rocks. F. V. Zaǐkovskiǐ and V. S. Bashmakova (All-Union Inst. of Min. Raw Materials, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (1), 50–54.—It is established that soln. of the complexes of arsenazo with rare-earth elements of the cerium and yttrium groups obey Beer's law. To determine total rare-earth elements, decompose the sample (0·025 to 0·25 g) by fusing with Na₂O₂, extract with hot water, filter off and wash the hydroxides, dissolve them in hot 5% HCl (20 to 30 ml), add saturated Na acetate soln. dropwise to pH 5 (Congo red) and dilute to 100 ml. Add 25% CaCl₂ soln. (0·5 ml) and 15 ml of a soln. of dioxalyl-acetone (≡ 4 g of oxalate ion), boil for 15 min., set aside overnight, and filter and wash the ppt. with 1% oxalic acid soln. Ignite the ppt. at 700°, evaporate the residue with 3 to 4 ml of conc. HCl, dissolve the chlorides (of the rare-earth elements, Th and Ca) in water (30 ml), neutralise to Congo red with 10% aq. NH₃, add HCl (sp.gr. 1·12) (0·5 ml) and a 0·1% soln. of thoron, stir, add 0·1 g of activated charcoal, stir and filter. Repeat the charcoal treatment; this removes Th and traces of Zr. To the filtrate add aq. NH₃ to pH 4, and make up to 50 ml. To an aliquot of this soln. (containing 5 to 70 μg of total rare-earth elements) add 1% ascorbic acid soln. (0·5 ml), 10% sulphosalicylic acid soln. (0·5 ml), 0·05% arsenazo soln. (3 ml) and 20% hexamine soln. (4 ml), make up to 25 ml, and after 30 min. measure the extinction at 570 mμ. A blank is prepared from an equal aliquot of the final soln., with the same additions except that

0·35 ml of a 10% tartaric acid soln. replaces the sulphosalicylic acid soln. The calibration curve is constructed from 25 ml of soln. containing 5 to 70 μg of total rare-earth elements, 5 μg of Ca, and the other reagents used in the analytical soln. described above; the blank contains all reagents but no rare-earth elements. The method permits the determination of 0·01 to 3% of rare-earth elements with errors of 5 to 20%.   C. D. KOPKIN

4319. Thermal decomposition of the rare-earth-metal oxalates. W. W. Wendlandt (Dept. of Chem. and Chem. Engng, Texas Technol. Coll., Lubbock, U.S.A.). *Anal. Chem.*, 1959, **31** (3), 408–410.—The oxalates of Tb, Dy, Tm, Yb and Lu were prepared as the 10-, 6- or 5-hydrates by homogeneous pptn. with methyl oxalate, and 70 to 90-mg samples were heated at 5·4° per min. on a thermobalance, in a slow stream of air; Tb and Dy form unstable intermediate hydrates; stable hydrate weight levels were obtained for Tm, Yb and Lu. The dihydrates are surprisingly stable, but the anhyd. oxalates decompose rapidly, liberating CO and CO_2. Losses in weight of the hydrates begin at 45° to 60°, and the oxides are finally obtained at 715° to 745°.
P. D. PARR-RICHARD

4320. Separation of rare-earth elements from beryllium, magnesium, zirconium, titanium, uranium and stainless steel. M. W. Lerner and L. J. Pinto (New Brunswick Lab., U.S. Atomic Energy Comm., N.J.). *Anal. Chem.*, 1959, **31** (4, Part I), 549–551.—Rare-earth elements present in metals to be used for nuclear technology must be isolated prior to their spectrographic determination, and detailed procedures are given for the separations cited above.   P. D. PARR-RICHARD

4321. Separation of iron from rare-earth elements. J. H. Křepelka, K. Vetejška and J. Mazáček (Res. Inst. Ores, Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (1), 198–202.—The separation of Fe from rare-earth metals on the strongly basic ion-exchange resin OAL has been investigated. The rare-earth elements and Th are not adsorbed from an HCl medium and can be determined in the percolate, whereas Fe is retained on the column and can be eluted and determined in the usual way. Zirconium is also retained on the column, but does not interfere. The procedure has been tested by analysing monazite concentrates. The sample is fused with an excess of Na_2O_2, washed with hot H_2O till neutral (removal of sodium phosphate), then dissolved in HNO_3. Iron, together with rare-earth metals, Th, Zr and Ni, is pptd. with aq. NH_3, the ppt. is washed with hot H_2O and dissolved on the filter with hot HCl. The soln. is then added to an OAL column previously washed with 8 N HCl; Fe is eluted with hot H_2O and determined volumetrically. Rare-earth elements and Th can be determined gravimetrically after pptn. with aq. NH_3 or oxalic acid.   J. ZÝKA

4322. Ion-exchange separation of cerium and thorium with lead - EDTA complex as eluting agent. Tomitsugu Taketatsu (Chem. Dept., Fac. of Sci., Kyushu Univ., Hakozaki, Fukuoka). *Bull. Chem. Soc. Japan*, 1959, **32** (3), 291–293 (in English).—The optimum conditions for this separation on Dowex-50 resin (NH_4^+ form) are a concn. of the lead - EDTA soln. of 0·015 M at a pH of 3·0 and a flow rate of 1·0 to 1·5 ml per min. Thorium ions are completely eluted with 200 ml of the eluent

under these conditions, while no cerium ions are detected in the eluate even after using 1 litre of the eluent. After elution of Th, the column is washed with water, and Ce is eluted with 3 N HCl.
I. JONES

4323. Spectrographic determination of small quantities of lanthanum, praseodymium, neodymium and yttrium in cerium. Pao-Lin Hsu, Lien-Fang Shen, Chien-Hwa Cheng and Ting-Chao Chang. *Acta Chim. Sinica*, 1958, **24** (6), 419–425.—Two methods for the determination of rare-earth-element impurities in "purified" cerium are described. (i) The sample is dissolved in HCl (1:19) so that the concn. of CeO_2 is 10 mg per ml. A drop of the prepared soln. is transferred to the flat top of a graphite electrode previously treated with liquid paraffin. The electrode is dried on a hotplate and is then excited in an a.c. arc (220 V, 5 amp.). A spectrograph ISP-51 (with UF-85 auto-collimating camera tube) is used, with a slit width of 0·01 mm. By using the line pairs La 4333·74 - Ce 4330·90, Pr 4225·33 - Ce 4229·63, Nd 4061·09 - Ce 4057·30, and Y 4374·94 - Ce 4376·88, La, Pr, Nd and Y can be determined quant. in the concn. ranges 0·055 to 0·62%, 0·089 to 1·29%, 0·052 to 0·59% and 0·025 to 0·40%, respectively. The coeff. of variation for single determinations are $\pm$ 4·7%, $\pm$ 10·8%, $\pm$ 7% and $\pm$ 7%, respectively. (ii) For cerium samples of high purity, ether extraction is used to remove most of the Ce and concentrate the rare-earth-element impurities. Because of its relatively simple spectrum, the element Y has been used as carrier and internal standard. The concentrate, in HCl soln. (concn. 1 mg of rare-earth oxide per ml) is excited and photographed by the same method as in (i). The line pairs used are La 4238·38 - Y 4235·73, La 3988·52 - Y 3951·60, Pr 4222·98 - Y 4235·73, and Nd 4232·38 - Y 4235·73. With a sample of 100 mg (1 mg of Y_2O_3 added as internal standard) the analytical sensitivities are 0·01%, 0·025% and 0·028% for La, Pr and Nd, respectively. The experimental error is $\simeq \pm 10\%$.
SCI. ABSTR. CHINA

4324. An anomalous change in the intensity of the samarium lines in the direct-current arc. R. R. Shvangiradze. *Optika i Spektroskopiya*, 1958, **5** (1), 88–90; *Ref. Zhur., Khim.*, 1959, (2), Abstr. No. 4310.—Experimental data are given of an anomalous change in the intensity of the spectral lines of Sm. A mixture of rare-earth-metal oxides and powdered carbon (1:1) was placed in a crater in a carbon electrode and ignited in a d.c. arc at 5 amp. It was found that the changes in the density of the lines, taken every 15 sec., were similar for all the rare-earth elements studied, with the exception of Sm. When the mixture contained mainly Sm, with small admixtures (0·02 to 0·1%) of the other rare-earth elements, at the end of the ignition of the Sm there was a sharp increase in the intensities of the lines of all the admixtures. This was not observed when any other rare-earth element was the main constituent. With increase of the current, the intensity of the rare-earth-element lines increases. The intensity of the Sm lines increases only up to a current of 6 amp., remaining almost constant thereafter. The conclusion is drawn that the anomalous behaviour of Sm is not due to processes taking place in the vapour cloud of the arc, but depends on an abnormal effect in the transfer of matter from the solid to the gaseous state. In the anode crater the Sm undergoes chemical changes which are different from those

of the other rare-earth metals. The vapour pressure of the samarium compounds entering the arc cloud is higher than that of the rare-earth elements. These anomalies are not observed in an a.c. arc between copper electrodes. On the basis of the results obtained, conclusions are drawn regarding the practical spectrographic determination of Sm and rare-earth-element admixtures in samarium concentrate.   C. D. KOPKIN

4325. Gravimetric determination of silica in fluorine-containing beryllium oxides. J. L. Huguet (Comisión Nacional de Energía Atómica, Buenos Aires). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/1580, 5 pp.—A study is made of the applicability of the Schernk and Ode method to the gravimetric determination of the SiO_2 content of technical-grade beryllium compounds which contain some fluoride by reason of their origin. It is found that the method gives good results in the range for which it has been tried ($\simeq 1\%$ of SiO_2).   NUCL. SCI. ABSTR.

4326. Hydroxyanthraquinones as reagents for germanium. I. M. Korenman, N. V. Kurina and E. A. Emelin. *Trudÿ po Khim. i Khim. Tekhnol.*, 1958, (1), 134–137; *Ref. Zhur., Khim.*, 1959, (1), Abstr. No. 933.—The colour reactions of $GeO_3{}^{2-}$ with 1:2:4:5:6:8-hexa- (**I**), 1:2:4-tri- (**II**), 1:5-di- (**III**), 1:4-di- (**IV**) and 1:2:5:8-tetra- (**V**) hydroxyanthraquinone are studied. A 0·01% soln. of the reagent in 95% H_2SO_4 is used. In all cases a colour is formed (the limiting dilution and the detectable minimum of Ge, in μg per 0·1 ml, are given in brackets)—with **I**, violet (1 in 7×10^4, 1·4); with **II**, red (1 in 5×10^4, 2·0); with **III**, orange, (1 in $3·5 \times 10^4$, 2·9); with **IV**, red (1 in 3×10^4, 3·3); and with **V**, violet (1 in $1·4 \times 10^4$, 7·0); **I**, **II** and **V** are the most selective of the reagents studied. Only $BO_3{}^{3-}$, Al^{3+} and Tl^+ interfere in the detection of Ge, since these also react with hydroxyanthraquinones. **I** and **IV** fluoresce in the presence of Ge, pinkish-red and clear yellow, respectively, this being noticeable even in ordinary light. The sensitivity of the fluorescent soln. is the same as for the corresponding colour reactions, but the selectivity is somewhat higher (Ge can be detected by **I** in the presence of twice the amount of Al). **I** can also be used for the photometric determination of Ge, measuring the extinction at $610 \, m\mu$.   C. D. KOPKIN

4327. Determination of germanium using the constant temperature d.c. arc method. M. Malinek (Metallurg. Inst., Czech. Acad. of Sci., Prague). *Appl. Spectroscopy*, 1959, **13** (1), 1–3.—Germanium, in a variety of matrices, at concn. from 0·01 to 1·0%, can be determined by means of a single working curve. The results for 16 replicate determinations on one sample gave a coeff. of variation of $\pm 11\%$.   K. A. PROCTOR

4328. Rapid method of determining germanium in coal ash. M. A. Menkovskiĭ and A. N. Aleksandrova (I. V. Stalin Moscow Mining Inst.). *Zavod. Lab.*, 1959, **25** (2), 161.—The sample (0·2 to 0·5 g) is decomposed by heating with 10 ml of syrupy H_3PO_4 for 20 to 30 min.; 10 ml of 6 N HCl is added, and $GeCl_4$ is distilled off into 5 to 6 ml of water. Further distillation is carried out after the addition of 10 ml of 6 N HCl. The distillate is diluted to 50 ml and Ge is determined colorimetrically in an aliquot by means of phenylfluorone in the presence of gelatin (*cf.* Nazarenko *et al.*, *Anal. Abstr.*, 1958, **5**, 3292).   G. S. SMITH

4329. Spectrographic method for quantitative determination of germanium in zinc ores and in metallurgical intermediate products. S. Witkowska (Inst. of Non-Ferrous Metall., Gliwice). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 471–475.—By means of spectrographic analysis the natural product was compared with a synthetic sample, similarly treated and corrected (*e.g.*, by addition of Al_2O_3, Ag_2O and As_2O_3) so as to be almost identical with the natural product. To 100-g portions of the synthetic sample, an appropriate amount of GeO_2, dissolved in 10% KOH soln., was added, and after drying at 105° the prepared standard was thoroughly homogenised for spectrographic examination. Two line-pairs were used, with Bi as internal standard—Bi 2938·30 A and Ge 2709·626 A, and Bi 2938·30 A and Ge 3039·064 A, the second being used when In was absent. Materials varying greatly in composition and volatility were examined by the total energy method. The curve for the line-pair Bi 2897·98 A - Ge 2657·178 A was satisfactory when compared with classical methods. It is concluded that the accuracy of the determination of Ge (0·001 to 0·05%) by the former (pellet) method is $\pm 6·2\%$ and by the total energy method $\pm 15·0\%$.   W. B. MIASKOWSKI

4330. Polarographic reduction of quadrivalent germanium in complexing organic acid solutions. M. Lucco Borlera (Ist. di Chim. del Politec., Torino, Italy). *Ric. Sci.*, 1959, **29** (1), 100–105.—The polarographic reduction of Ge^{4+} is investigated with salicylic, oxalic and tartaric acids as complexing agents. The optimum pH range for reduction is—HCl - salicylic acid, 7·5 to 9; HCl - oxalic acid, 7 to 9; HCl - tartaric acid, 8·2 to 9·5. The values of the diffusion current constants obtained in various media are listed and the optimum pH range is given over which the reduction is of analytical value. The best complexing acid is salicylic, with a 0·001 M Ge^{4+} soln.   L. ZANONI

4331. Determination of copper admixtures in metallic germanium by activation analysis. J. Gottfried and J. V. Jakovlev (Res. Inst. Inorg. Chem., Ústí Nad Labem, Czechoslovakia). *Chem. Průmysl*, 1959, **9** (4), 179–182.—The sample is irradiated in a nuclear reactor by means of a stream of neutrons (5×10^{11} to 2×10^{13} neutrons per sq. cm per sec.) for 48 hr. and then dissolved in a mixture of HCl and HNO_3. Arsenic, Cu, Zn, Mo, Te, Sb and Ce are added as carriers; Ge and As are separated by distillation, Te by a stream of SO_2 (reduction), Sb and rare-earth elements as hydroxides, Mo with benzoin α-oxime from a soln. in HCl and Cu by pptn. from a slightly ammoniacal soln. with the same reagent. The quant. separation of Cu from Zn is achieved by further pptn. with H_2S and finally as CuSCN, the activity of which is then measured.   J. ZÝKA

4332. Determination of small amounts of lead in rocks. Z. A. Baskova (All-Union Scientific-Res. Geol. Inst., Leningrad). *Zhur. Anal. Khim.*, 1959, **14** (1), 75–80.—The concentration of Pb by the following methods is described, the percentage of Pb extracted being given—(*i*) extraction with dithizone and $CHCl_3$ (91%); (*ii*) co-pptn. with HgS (60 to 70%); (*iii*) co-pptn. with ZnS (80 to 90%); (*iv*) co-pptn. with $BaSO_4$ (76%); (*v*) extraction of Pb diethyldithiocarbamate with amyl alcohol and toluene (1:1) (97%); and (*vi*) distillation of Pb in the presence of C *in vacuo* or in a stream of N (80 to 100%). The percentage extractions were

mainly found radiochemically, the final determinations of Pb being made polarographically or colorimetrically with dithizone.   C. D. KOPKIN

4333. Spectrographic analysis of lead- and zinc-type alloys. N. A. Kiseleva. *Poligr. Proizvodstvo,* 1958, (6), 23–25; *Ref. Zhur., Khim.,* 1959, (1), Abstr. No. 1001.—The spectra are excited in a condensed spark discharge from an IG-3 generator. The electrodes are prepared from the analytical samples and are 6 mm in diam. rounded to a hemisphere. The analytical conditions are—capacity $0.005\ \mu F$, self-induction $0.01\ mH$, spark gap 2 mm, current 0·8 amp., sparking 1 min., exposure 1 min. The spectra are photographed in a medium spectrograph with a slit width of 0·03 mm. Calibration curves are constructed on the co-ordinates $\triangle S$ *vs.* log *C*, from the lines (in A) Sb 2598 and Pb 2628, Sn 2429 and Pb 2446, and Cu 3274, Zn 3345, Ni 3414 or Al 3082 and Pb 3220. The analysis takes 50 min. When determining Al, Mg and Cu in zinc alloys from the lines at Al 3082·1, Mg 2790·7, Cu 3247·5 and Zn 3075·9 A, the condensed spark discharge from the generator in a simple circuit was used (capacity $0.005\ \mu F$, self-induction 0, current 2 amp., sparking 30 sec., exposure 30 sec., slit width, 0·08 mm). Lead, Cu, Sb and Sn are determined by exciting the spectra in an a.c. arc discharge with an interrupter and a threefold attenuator. The electrodes are ground to a flat surface. The arc gap is 2·5 mm, current 7 amp., ignition 1 min., exposure 1 to 3 min., and slit width 0·04 mm. The analytical lines (in A) are Cu 3247·5 and Zn 3075·9, Pb 2833·1 and Zn 2712·5, Sb 2528·5 and Zn 2712·5, Sn 3175·0 and Zn 2712·5. The analysis takes 50 min. The standards are prepared by fusion of the pure metals.   C. D. KOPKIN

4334. Chromotropic acid derivatives as reagents for titanium. I. M. Korenman, F. S. Frum and L. V. Ryzhkova. *Uch. Zap. Gor'kovsk. Univ.,* 1958, (32), 113–117; *Ref. Zhur., Khim.,* 1959, (1), Abstr. No. 937.—The possible use of a number of chromotropic acid azo dyes as colour reagents for Ti^{4+} is studied. The dyes are the azo derivatives of chromotropic acid with $HO(Cl)C_6H_3-$ (**I**), $HO_3S(OH)C_6H_3-$ or $HO_3AsC_6H_4-$. All the dyestuffs studied are water soluble, giving soln. which may be kept for a long period without change. The addition to 1 ml of a soln. of $TiOSO_4$ of 5 drops of a satd. soln. of Na acetate and 3 drops of a 0·1% soln. of a dyestuff produces a coloured ppt. in the presence of large amounts of Ti, or a coloured soln. with low concn. of Ti. It is established photometrically that the formation of the coloured product requires 2 moles of **I** per g of Ti. The most sensitive reaction is found with **I** (limiting dilution 1 in 1×10^6); no interference is caused by Mg, Ca, Pb or other elements. Small amounts of Ti should be determined photometrically with **I** at $550\ m\mu$ in a 10-mm cell. To 3 ml of weakly acid test soln. add *M* Na acetate (3 ml) and a 0·2% soln. of **I** (3 drops). With 10 to 60 μg of Ti in 3 ml, the intensity of the colour is proportional to the concn. of Ti.
                C. D. KOPKIN

4335. Study of certain azo dyes as reagents for titanium. F. S. Frum and E. P. Trushina. *Uch. Zap. Gor'kovsk. Univ.,* 1958, (32), 119–125; *Ref. Zhur., Khim.,* 1959, (1), Abstr. No. 938.—The colour reactions of Ti^{4+} with 10 azo dyes are studied. The most sensitive reagent is $O_2N(Cl)(OH)C_6H_3-$ $N:N\cdot C_{10}H_5(OH)SO_3Na$ (**I**) which with Ti forms a sol. pink complex of composition $Ti:\mathbf{I} = 1:2$. The

limiting dilution is 1 in 2×10^6. For the detection of Ti with **I**, to 1 ml of weakly acid test soln. add a saturated soln. of Na acetate (5 drops) and a 0·2% soln. of **I** (2 drops); no interference is caused by W, Be, La or Fe. In the presence of Th, Ce, Zr or Mo, the use of $HO_3S(NH_2)(OH)C_{10}H_4\cdot N:N\cdot(C_6H_4)_2\cdot N:-N\cdot C_6H_3(OH)COOH$ is recommended, and in the presence of Cr, UO_2^{2+}, Al, Zn or Ca, the reagent $HO_3S(NH_2)(OH)C_{10}H_4\cdot N:N\cdot C_6H_4\cdot N:N\cdot C_6H_3(OH)-COOH$. For the photometric determination of Ti, to 5 ml of test soln. add a 0·2% soln. of **I** (0·35 ml) and a satd. soln. of Na acetate (0·75 ml), and measure the extinction with a green filter. The attenuation of the colour of the soln. is proportional to the content of Ti with 5 to 50 μg of Ti in 5 ml. The photometric method also gives completely satisfactory results in the presence of Mg, Ca, Mn, Al and Fe.   C. D. KOPKIN

4336. Determination of titanium with EDTA. D. H. Wilkins (General Electric Co., New York, U.S.A.). *Anal. Chim. Acta,* 1959, **20** (2), 113–116.—The method of back-titration with Cu^{2+} (*cf.* Šír and Přibil, *Anal. Abstr.,* 1957, **4**, 822) fails through the pptn. of hydrated TiO_2. This pptn. is now prevented by the addition of H_2O_2. *Procedure*—To the soln. of $\simeq 10$ mg of Ti in HCl or HF add 10 ml of dil. H_2SO_4 (1 + 1) and evaporate to fuming. Cool to room temp., add 10 to 15 g of ice and 3 drops of H_2O_2 soln. (30 vol.). Add a 5 to 10-ml excess of standard EDTA soln., dilute to 100 ml, add NaOH soln. (50%) to produce a pH of 4 to 5, and 8 drops of 1-(2-pyridylazo)-2-naphthol indicator soln. (0·05% in ethanol). Titrate with a standard soln. of Cu^{2+} to a change from orange to orange - red. The max. error recorded is -0.08 mg.
                H. N. S.

4337. Extraction of titanium thiocyanate with tri-*n*-octylphosphine oxide. Direct colorimetric determination in the organic phase. J. P. Young and J. C. White (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.,* 1959, **31** (3), 393–397.—Titanium thiocyanate is extracted from acid SO_4^{2-} and Cl⁻ soln. with tri-*n*-octylphosphine oxide in *cyclo*hexane and the absorption is measured at 432 mμ. Beer's law is followed up to 1·7 μg of Ti per ml, and the molar absorption coefficient is $\simeq 41,000$. Neither quadrivalent metal ions nor large quantities of Fe^{3+} or of U^{6+} interfere; Nb in threefold excess over the Ti gives a 5% error. Fluoride, PO_4^{3-} and oxalate do not interfere, but NO_3^{-} cause decomposition of the SCN⁻. Recoveries are generally > 95% and the coefficient of variation is $\simeq 2\%$. Twenty-five diverse ions were tested for interference.
                G. P. COOK

4338. Rapid method of determining hydrogen in metallic titanium powder. R. N. Rubinshtein and N. G. Mendlina. *Zavod. Lab.,* 1959, **25** (1), 34–36.—A simple apparatus for the vacuum extraction at 600° to 700° and determination of H is described.
                G. S. SMITH

4339. Preparation and analysis of titanium -hydrogen standard samples. M. J. Trzeciak (Battelle Memorial Inst. Defense Metals Information Center, Columbus, Ohio). *U.S. Atomic Energy Comm.,* Rep. DMIC-Memo-9, 1959, 14 pp.—The preparation of standard Ti - H samples for use in standardisation and the evaluation of analytical methods for gases in metals is given. The preparation of materials and the hydridation procedure are described, and the results of sample analyses are compared with those of other laboratories.   NUCL. SCI. ABSTR.

4340. Chemical and spectrochemical analysis of zirconium and Zircaloy. G. W. Goward and R. M. Jacobs (Westinghouse Electric Corp. Bettis Plant, Pittsburgh). *U.S. Atomic Energy Comm.*, Rep. WAPD-BT-11, pp. 81–103.—The development and use of chemical and spectrochemical procedures at the Bettis Plant for the analysis of zirconium and Zircaloy alloys are described. In addition, the establishment of certain reference standards, some of the difficulties encountered in the analysis, and plans for resolving the difficulties are discussed.

NUCL. SCI. ABSTR.

4341. Determination of zirconium in plutonium by ion exchange and spectrography. R. Ko (Gen. Electric Co., Richland, Wash., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (1), 10–11.—Plutonium can be separated from Zr by retaining it as the nitrate complex on Dowex-1 anion-exchange resin, and collecting the Zr in the percolate and wash soln.; Zr is then determined, after evaporation of the soln., by graphite spark excitation, with Co as the internal standard. Concn. as low as 20 p.p.m. of Zr have been determined with a precision of $\pm 17\%$ for a single determination. K. A. PROCTOR

4342. Spectral analysis of impurities in zirconium and its compounds. Y. I. Korovin and L. V. Lipis. Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/2137, 15 pp.—A study was made of a direct spectral method, with high sensitivity and reasonable accuracy, for the simultaneous determination of 24 elements in zirconium and its compounds. The method is based on the use of a discharge in a hollow cathode. The temp. of the sample, which is under constant discharge conditions, is unambiguously related to the discharge current. This makes it possible to considerably reduce the influence of the third components in determining a large group of elements owing to a more complete application of the fractional evaporation principle. With many elements it is possible to use direct density measurement owing to the high stability of the source of light, while in other instances the use of an internal standard considerably improves the calibration curves and the reproducibility of results. The method is quicker and more labour-saving than the conventional methods; it is possible to determine the impurities in zirconium with high sensitivity, and such determinations, although not optimum, meet the requirements for the quality of zirconium and its compounds. NUCL. SCI. ABSTR.

4343. Spectrochemical determination of residual hafnium in zirconium and zirconium alloys using d.c. arc excitation and a barium fluoride flux. G. J. Harter and R. F. Farrell (Westinghouse Electric Corp. Bettis Plant, Pittsburgh, Pa.). *U.S. Atomic Energy Comm.*, Rep. WAPD-CTA(GLA)-162-10, 1958, 6 pp.—This method is used to determine residual Hf in zirconium and Zircaloy from 30 p.p.m. up to 300 p.p.m. By selection of suitable line pairs the method may be extended to include other concn. ranges. The oxidised sample is mixed with a BaF_2 - graphite mixture (1 : 1) and pressed into an electrode (0·25 in. diam., 2 mm deep). Excitation of the sample is provided by high-current d.c. arc. Intensity ratios are calculated for the analytical line pairs and concn. determined from working curves.

NUCL. SCI. ABSTR.

4344. Thermogravimetry of analytical precipitates. LXVI. Determination of hafnium. A. Dautel and C. Duval (École Nat. Supérieure de Chim., Paris, France). *Anal. Chim. Acta*, 1959, **20** (2), 154–159 (in French).—Various precipitants are used for Hf^{4+} and the resulting compounds are examined with the thermobalance to find the most suitable means of gravimetric determination. The following reagents yield ppt. that must be ignited to HfO_2, and the minimum ignition temp. are indicated—aq. NH_3, 350°; air charged with NH_3, 500°; tannin, 655°; p-hydroxyphenylarsonic acid, 660°; cupferron, 670°. When pptd. as phosphate, HfP_2O_7 is obtained on heating the product to 750°. The basic selenite obtained by pptn. with $SeO_3{}^{2-}$ is of variable constitution until it is decomposed to HfO_2 at 680°, but if the ppt. is digested at 80° it becomes $Hf(SeO_3)_2$ which is stable at 90° to 220°. The ppt. obtained with mandelic acid is $Hf(C_6H_5 \cdot CHOH \cdot CO_2)_4$, which is stable at 90° to 260° and yields HfO_2 at 500°. The normal selenite and the mandelate are the preferred compounds.

H. N. S.

4345. Extraction of thorium by a mixture of ethyl acetate and acetone. M. Andjelković and D. Rajković (Inst. for Technol. of Mineral Raw Materials, Belgrade). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/474, 10 pp.—The extraction is applicable to a wide range of Th concn. The method for the determination of Th is particularly efficient for materials with a low Th content, using extraction with ethyl acetate - acetone as the separation method and Thomason's colorimetric method for the final determination. When the material contains larger amounts of Th, the final determination can be carried out by the gravimetric method. Besides Th, only U, Zr and B were extracted among all the elements analysed. To avoid difficulties with Zr, the Zr is complexed with tartaric acid and is not then extracted. Uranium is extracted quant., but during the determination of Th with thoron it can be present in 25-fold excess without the error exceeding 5%. Bismuth does not interfere. The method is simple, sufficiently rapid, and applicable to routine work. From materials with a complex composition, microgram quantities of Th can be determined with an error usually $< \pm 5\%$. NUCL. SCI. ABSTR.

4346. Determination of thorium in low-grade ores. A. E. Suñer (Comisión Nacional de Energía Atómica, Buenos Aires). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/1581, 26 pp.—The analytical procedure used for separating interferences has a separation factor (quotient of the amount of interference before and after using the procedure) of 10^4. It consists in pptg. the Th with HF, digesting with Na_2CO_3, extracting the Th with diethyl ether, pptg. as iodate in an oxalic acid medium with a silver carrier ion, and spectrophotometric measurements with alizarin red S (C.I. Mordant Red 3). The complete recovery of Th, in each of the steps of the analysis, has been verified by using ^{234}Th, as well as by spectrophotometry and gravimetry. The method was applied to the analysis of some minerals with satisfactory results. NUCL. SCI. ABSTR.

4347. Quantitative analysis of thorium in minerals and thoriferous products by a method based on radioactivity. R. Collee, J. Govaerts and L. Winand (Univ. of Liége). Second U.N. International

Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/1701, 15 pp.—A brief résumé of the classical methods of quant. determination of Th in ores and thoriferous products is given to show that a rapid, accurate and precise physical method based on the radioactivity of Th would be of great use. A method based on the use of the characteristic spectrum of the thorium γ-radiation is presented. The preparation of the samples and the instruments needed for the measurement are discussed. The experimental results are reproducible and it is possible to detect Th contents of $<1\%$.   Nucl. Sci. Abstr.

4348. Determination of thorium in monazite ore by means of EDTA. I. Separation of thorium by precipitation with sodium iodate. Saburo Kitahara and Shin Hara (Sci. Res. Inst., Tokyo). *Rep. Sci. Res. Inst., Tokyo*, 1957, **33**, 340–342.—To the soln. obtained by decomposing monazite ore with H_2SO_4 add oxalic acid to transform Zr and Ti into complexes and then add $NaIO_3$ to precipitate Th. In this procedure a small quantity of Th remains in the soln. and considerable quantities of rare-earth elements are co-pptd. with thorium iodate. **II. Titration of thorium, with catechol violet as indicator.** Shin Hara and Saburo Kitahara. *Ibid.*, 1957, **33**, 343–349.—Decompose monazite ore with H_2SO_4 and add $NaIO_3$ in the presence of 2% oxalic acid and 3 N HNO_3 until its concn. is $>8\%$, then cool. This procedure precipitates almost all the Th as the iodate even if large quantities of $SO_4{}^{2-}$ are present. Dissolve the thorium iodate in dil. HNO_3; decompose the oxalic acid with $KMnO_4$; decompose the $NaIO_3$ and the excess of $KMnO_4$ simultaneously with hydroxyammonium chloride. Then determine Th by titration with EDTA, with catechol violet as indicator. Rare-earth elements, even in large quantities, do not interfere. Zinc does not interfere if large quantities of rare-earth elements are not also present. Avoid the interference caused by Fe^{3+}, Al^{3+}, $PO_4{}^{3-}$ and $SO_4{}^{2-}$ by re-pptg. the thorium iodate.   Chem. Abstr.

4349. Sodium hypophosphate as a reagent for the separation of thorium, zirconium and niobium. L. Kosta and L. Ravnik (J. Stefan Inst., Ljubljana, Yugoslavia). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/482, 11 pp.—A selective procedure for the separation of Nb, Zr and Th from most elements has been devised. It is based on the pptn. of these elements with sodium hypophosphate, with Ti as carrier. The pptn. from 6 N HCl is nearly quant. After eliminating other interfering elements, Th is separated as the fluoride. Zirconium is co-pptd. as barium zirconium fluoride from a soln. in which Nb is complexed with HF. Niobium is finally isolated from the HF medium as the cupferrate. A detailed description of the procedures for the determination of the isolated ions is given. A liquid - liquid extraction system with mesityl oxide as solvent for separating Nb from the HCl - HF medium is described, and data for the distribution coeff. are included. The advantage of this system over others is that it requires a low concn. of HF.   Nucl. Sci. Abstr.

4350. Rapid method for determining the concentration of ammonium sulphate solutions. J. R. Whitaker and R. Hughes (Dept. of Food Technol., Univ. of California, Davis, U.S.A.). *Nature*, 1959, **183**, 603–604.—From refractive index measurements of soln. of $(NH_4)_2SO_4$, the following equation,

which avoids the necessity for density determinations, was developed—

$$Y = 0.0403 + 41.1(RI_1 - RI_2) + 309(RI_1 - RI_2)^2.$$

where Y is the molarity of the $(NH_4)_2SO_4$ soln., and RI_1 and RI_2 are the refractive indices of the soln. and of water, respectively. The temp. need not be known, and the over-all accuracy is $\pm 1.0\%$ in the range 0.50 to 4.06 M. The sensitivity can be increased 10-fold by the use of an immersion refractometer, but the Abbé refractometer is adequate for soln. used for gradient elution and protein pptn.   S. Baar

4351. Colour test for the detection of hyponitrites. J. Veprek-Šiška, V. Pliška and F. Šmirous (Dept. of Inorg. Chem., Tech. Univ., Prague, Czechoslovakia). *Analyst*, 1959, **84**, 119.—The test for hyponitrites described by Corbet (*Biochem. J.*, 1934, **28**, 1577) and by Rao and Rao (*Analyst*, 1938, **63**, 718) is investigated to determine its specificity and the optimum conditions for its application. It was found that the colour produced by reaction of hyponitrites with resorcinol and KIO_4 in acid soln. is not specific for hyponitrites but is for nitrites. The absorption spectrum of the red soln. has a characteristic maximum at 513 mμ, the position of which is independent of pH, but the extinction decreases with increasing pH. Other compounds of N that are oxidised by KIO_4 to nitrite therefore produce the same colour reaction with resorcinol and KIO_4 as does hyponitrite. As this, the only published reaction for hyponitrite, proves to be a reaction for nitrite, it is not possible to identify small amounts of hyponitrite formed in the presence of nitrite, oxyhyponitrite or hydroxylamine.   A. O. Jones

4352. Modality of the isotope dilution method of chemical analysis applied to the determination of phosphorus. J. M. Arriaga e Cunha and J. Baptista (Estação Agrónom. Nacional, Sacavém, Portugal). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/2332, 9 pp.—A constant amount of P is pptd. from two aliquots of an unknown labelled phosphate soln. to one of which a known wt. of inactive P is added. From the activities remaining in the supernatant soln., and from the wt. of P in the ppt., the P content of the soln. is calculated. The results obtained by the proposed method for the determination of P in a soln. with a known concn. of the element agreed closely with those obtained with the same soln. by the colorimetric method of Allen. The accuracy of the method must be checked when the determination of P by conventional methods is difficult.   Nucl. Sci. Abstr.

4353. Potentiometric determination of phosphate ions. Z. I. Ivanova and P. N. Kovalenko (Rostov-Don State Univ.). *Zhur. Anal. Khim.*, 1959, **14** (1), 87–90.—Phosphate ions are determined by potentiometric titration with $Hg(NO_3)_2$ soln. with a mercury indicator electrode. With decrease of concn. of $PO_4{}^{3-}$ the error increases, $e.g.$, from $+ 0.7\%$ with 28.4 mg of $PO_4{}^{3-}$ per ml to $- 20.3\%$ with 2.6 mg per ml, with 0.161 N $Hg(NO_3)_2$; satisfactory results (error $\gtrless 2\%$) are obtained with $\not< 5$ mg of $PO_4{}^{3-}$ per ml. The addition of ethanol decreases the error. The presence of colloidal substances (in soil extracts) does not influence the results. The errors in determining small concn. of $PO_4{}^{3-}$ are much reduced by using the method of

double additions (*i.e.*, titrating, adding more phosphate soln. in two portions and titrating after each addition). The presence of 100-fold amounts of Cl^- does not cause interference. Phosphate and Cl^- can be determined successively. No interference is caused by the presence of Ca^{2+}, Mg^{2+}, Ba^{2+} or SO_4^{2-}. The pH of the soln. may be in the range 3 to 10. The method has been tested on minerals. C. D. KOPKIN

4354. Paper chromatography of polyphosphates. E. Heinerth (Henkel & Cie., Düsseldorf, Germany). *Z. anal. Chem.*, 1959, **166** (1), 37–39.—After separation of the phosphates by ascending chromatography with ethanol - water - trichloroacetic acid (80 ml; 20 ml; 5 g) and a little aq. NH_3, the bands, revealed by spraying with ammonium molybdate, drying, and spraying with a reducing soln., are cut out. The paper is destroyed by boiling with $HClO_4$, and the phosphates are hydrolysed by boiling the diluted soln. and determined spectrophotometrically. G. BURGER

4355. Analytical chemistry of the fluorophosphates. R. Klement and K. O. Knollmüller (Inst. f. anorg. Chem., Univ., München). *Z. anal. Chem.*, 1959, **166** (3), 193–201.—Phosphate, FPO_3^{2-} and $F_2PO_2^-$ may be detected in the presence of one another by paper electrophoresis in a buffer at pH 7. In the absence of any pptg. reagent, two spots are formed, one containing PO_4^{3-} and the other the fluorophosphate ions. If the initial soln. is spotted on a strip impregnated with uranyl acetate, PO_4^{3-} do not migrate. If the strip is impregnated with Pb acetate only $F_2PO_2^-$ migrate. Mixtures of PO_4^{3-} and fluorophosphates may be analysed by pptn. of Ag_3PO_4, filtration, removal of Ag^+ from the filtrate by ion exchange, boiling the eluate with HNO_3 and determining the PO_4^{3-} formed. T. R. ANDREW

4356. Chemical microscopy of inorganic phosphorus - nitrogen compounds. Identification by their o-tolidine, ammonium and silver salts. M. L. Nielsen and W. W. Nielsen (Res. and Engng Div., Monsanto Chemical Co., Dayton, Ohio, U.S.A.). *Microchem. J.*, 1959, **3** (1), 83–90.—Directions are given for the preparation of the *o*-tolidine, ammonium and silver salts of phosphoramidic, phosphorodiamidic (**I**), tri- and tetra-phosphenimidic acids. Eighteen photographs are given of the crystals, and it is shown that the tolidine salts serve for the identification of all the compounds except **I**, even in mixtures. Ammonium and silver salts are useful for the identification of **I**, and for the supplemental identification of the other compounds named. The effect of added substances such as decomposition products has not been studied, but it is noted that the absence of typical crystal forms must not be construed as indicating the absence of the species from the sample. R. E. ESSERY

4357. Analytical applications of the reaction between sodium arsenite and ferricyanide catalysed by osmium tetroxide. F. Solymosi (Inst. Inorg. and Anal. Chem., Univ., Szeged, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **16** (3), 267–278 (in English).—*Cf. Magyar Kém. Foly.*, 1956, **62** (9), 318; *Anal. Abstr.*, 1957, **4**, 1214. W. J. BAKER

4358. New (crystal phosphor) luminescence method of microchemical analysis. I. Detection of antimony. K. P. Stolyarov and N. N. Grigor'ev (A. A. Zhdanov Leningrad State Univ.). *Zhur. Anal. Khim.*, 1959, **14** (1), 71–74.—*The detection of*

Sb on ignited CaO.—The method is based on the formation of the crystal phosphor CaO.Sb, by igniting a bead of damp $CaCO_3$ in a platinum or nichrome loop and adding a drop of test soln. On igniting in a flame and inspecting in u.v. light, a greenish-yellow luminescence is observed if Sb is present. The method will detect 1×10^{-6} µg of Sb at a limiting dilution of 1 in 1×10^{10}. *The detection of Sb with $K_4Fe(CN)_6$*—This is based on the formation of the phosphor $K_4Fe(CN)_6$.Sb, and is best carried out by drying a spot of reagent soln. on a watch-glass, adding a drop of the test soln. to the hot dry spot, and allowing to dry. The crystals formed luminesce with a yellow colour in u.v. light; the detectable minimum is 0·001 µg of Sb, at limiting dilution of 1 in 1×10^7. Only As gives an analogous reaction (detectable minimum, 0·12 µg, limiting dilution 1 in $8·3 \times 10^4$). Since many elements form ppt. with $K_4Fe(CN)_6$, the Sb should first be extracted from HCl soln. with diethyl ether. C. D. KOPKIN

4359. Vanadametry. Determination of tervalent antimony: use of iodine chloride catalyst. K. Bhaskara Rao (Dept. of Chem., Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1959, **165** (3), 195–197 (in English).—Tervalent Sb is quant. oxidised with sodium vanadate in N H_2SO_4 in the presence of ICl as catalyst. It is shown that this reaction is completed in 5 min. at 98° to 100°. The excess of vanadate is then titrated with $FeSO_4$ soln. B. B. BAUMINGER

4360. Spectrographic analysis of type-metal for its antimony and tin content. V. T. Ivanova and E. M. Afanas'eva. *Sb. Trud. Vses. Nauch.-Issled. Inst. Goznaka*, 1957, (1), 236–242; *Ref. Zhur. Khim.*, 1959, (1), Abstr. No. 1002.—Use the sample as a cylindrical rod ground to a flat surface. Excite the spectra with a carbon upper electrode in an a.c. arc discharge at 4 to 5 amp. with an arc gap of 2 mm. To prevent fusion of the test alloy, include in the transformer circuit an interrupter so that the time of arcing is 0·04 sec. with an interval of 0·1 sec. Photograph the spectra in a medium spectrograph with a slit width of 0·015 mm and an exposure of 10 sec. Construct calibration curves from the lines (in A) Sb 2877·9 and Pb 2873·3, Sn 2850·6 and Pb 2873·3. The determinable concn. are Sb from 6 to 13% and Sn from 2 to 7%. Prepare standards by fusion of the pure metals at 500°, with subsequent chemical analysis. The choice of analytical lines and the conditions of the discharge are studied. The analysis takes 30 min. C. D. KOPKIN

4361. Determination of bismuth in lead and lead cable-sheathing alloys. J. H. Thompson and B. W. Peters (Materials Section, Test and Inspection Branch, P.O. Engng Dept., Fordrough Lane, Birmingham, England). *Analyst*, 1959, **84**, 180–182.—The finely divided sample is dissolved in dil. HNO_3 (1:2), the soln. is reduced to the lowest practicable bulk and is then boiled with HCl (70 ml); HBr is carefully added until the evolution of Br ceases, the cooled diluted liquid is filtered and the washed $PbCl_2$ ppt. is discarded. The filtrate is adjusted to 4 to 6 N with HCl and the residual Br is extracted with CCl_4. The aq. layer is then extracted with a soln. of diethylammonium diethyl-dithiocarbamate soln. in $CHCl_3$ (4 to 6 $\times$ 10 ml), an oxidising mixture of H_2SO_4, HNO_3 and $HClO_4$ is added to the combined extracts, the liquid is evaporated to fuming-point and finally heated to copious fuming. To the cooled digest are added

water (1 to 2 ml), tartaric acid (5 g) and 20 ml of dil. HNO_3 (1:15), and, when the tartaric acid is dissolved, 20 ml of thiourea soln. [10% in dil. HNO_3 (1:15). After adjustment to a known vol. with the thiourea soln. the extinction is measured at 470 mμ against water and referred to a calibration graph. Results are good in the range 0·002 to 0·06%.   A. O. JONES

4362. Organic reagents for salts of quadrivalent vanadium. I. M. Korenman, V. G. Potemkina and L. A. Trusova. *Uch. Zap. Gor'kovsk. Univ.*, 1958, (32), 109–111; *Ref. Zhur., Khim.*, 1959, (1), Abstr. No. 944.—A number of chromotropic acid azo dyes are studied as reagents for V^{IV}. The most sensitive reactions are found with dyes of the composition $(HO_3S)_2(OH)_2C_{10}H_3N:NR$, where R is $HO(Cl)C_6H_3$– (**I**), $HO_3SC_6H_4$– (**II**) or $H_2NC_6H_4$– (**III**). For the detection of V^{IV}, add 0·5 ml of 2 N aq. NH_3 to 2 ml of test soln. containing 0·1 mg of V, centrifuge off the ppt. comprising accompanying cations with some metavanadate, acidify the clear centrifugate with acetic acid, add 10 to 15 mg of cryst. hydrazine sulphate to reduce VO_3– to VO^{2-}, 1 drop of a 0·1% aq. soln. of reagent and 0·2 ml of 25% hexamine soln. The limiting dilution is 1 in 4 × 10^6. Reagent **III** is the most specific. The detectable minimum when using **I**, **II** or **III** is 0·25 μg of V per ml. None of the dyes studied reacts with metavanadate. The possibility is shown of using these reagents for the colorimetric determination of 20 to 100 μg of V per ml.   C. D. KOPKIN

4363. Coulometric titration with quinquevalent uranium. Determination of vanadium(V). S. L. Phillips and D. M. Kern (Dartmouth Coll., Hanover, N.H., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (3), 295–298.—A procedure is given for the determination of milligram amounts of V^V by titration with electrolytically generated U^V at pH 1 to 2·5 in an atmosphere of N. The end-point is determined amperometrically by a series of small increments of current. The apparatus is similar to that used for the titration of Fe^{3+} with U^V (*cf.* Edwards and Kern, *Anal. Abstr.*, 1957, **4**, 1828). The error is $\simeq \pm 0.3\%$; concn. as low as 15 μg can be titrated. Titrations of mixtures of Fe^{III} and V^V can be made at pH 1·5, both ions being reduced simultaneously.
                                    W. J. BAKER

4364. Decomposition of niobium-bearing ores and rocks. Aspects of the determination of niobium by thiocyanate. G. H. Faye (Dept. Mines Tech. Surveys, Ottawa). *Chem. Canada*, 1958, **10** (4), 90–96.—The decomposition of Nb-bearing ores and rocks by fusion with bisulphate and the subsequent photometric determination of the Nb with thiocyanate gives low results in the presence of U. Acid attack with HF - HCl - H_3PO_4 is faster, gives accurate results in the presence of U, and offers a number of other advantages. To a 0·1 to 2-g sample in a platinum dish add approx. 15 ml of 48% HF, 10 ml of conc. HCl and 1 to 2 ml of H_3PO_4. Evaporate the mixture to a paste. Cool and wash into a volumetric flask with M tartaric acid, filtering if necessary. Dilute with M tartaric acid and use aliquots for colour development by the method of Ward and Marranzino (*cf. Anal. Abstr.*, 1955, **2**, 3340).   CHEM. ABSTR.

4365. Determination of sulphur in mixtures of sodium, potassium and magnesium chlorides. E. Booth and T. W. Evett [U.K.A.E.A. (Research Group), C.37, Royal Arsenal, Woolwich, England]. A.E.R.E. Analytical Method AERE-AM 5, 1959,

6 pp.—The method is based on that of Luke (*Anal. Chem.*, 1949, **21**, 1369). The S is converted into H_2S by a mixture of HI and H_3PO_2 in a special apparatus (illustrated) and then distilled into a soln. of Zn acetate. The S is then determined colorimetrically after reaction with HCl, p-phenylenediamine and $FeCl_3$ for 30 min. The extinction of the soln. is measured at 595 mμ and the content of S is derived from a standard curve. The error should not exceed $\pm 5\%$ and the method is suitable for the determination of 5 to 40 μg of S. It is essential to work in a sulphur-free atmosphere, as atmospheric contamination is difficult to avoid.
                                    G. J. HUNTER

4366. Quantitative determination of traces of sulphides. E. Hoffmann (Div. of Building Res., C.S.I.R.O., Melbourne, Australia). *Z. anal. Chem.*, 1959, **166** (3), 168–170 (in English).—The apparatus described comprises two small reaction vessels joined by a U-tube containing water. To each vessel, one containing the specimen and sodium azide soln., and the other containing only sodium azide soln., add iodine soln., and shake the apparatus gently. The vol. of N evolved in the tube containing the sample is proportional to the amount of S^{2-} present, and is measured as the difference in pressure in the two reaction vessels shown by the difference in the water levels of the two arms of the U-tube. This has been directly related to S^{2-} concn. for 0·05 to 0·6 μg of S^{2-}. A precision of $\pm 25\%$ is claimed.   T. R. ANDREW

4367. Determination of sulphur in pyrites concentrates, and the possibility of determining sulphur in volatile organic and inorganic substances. Z. Rezáč and K. Straka (Forschungsinst. f. anorg. Chem. u. d. Verein f. chem. u. metallurg. Produktion, Ústí nad Labem, ČSR). *Z. anal. Chem.*, 1959, **166** (3), 161–168.—The finely ground sample (0·5 g) is mixed with 4 g of powdered manganese dioxide (containing 10% of KOH) in a porcelain crucible, then covered with a further 2 g of manganese dioxide and heated, first at $\simeq 400°$ for 10 min. and then in a furnace for 15 min. at 800°. The cooled crucible and contents are boiled briefly with water, and the liquid is diluted to 250 ml and filtered through a dry paper into a dry beaker; the first fraction is rejected. An aliquot (50 ml) of the remainder is passed through a Wofatit P ion-exchange resin column (H$^+$ form) at a rate of 10 ml per min. The column is washed twice with water and the percolate and washings are titrated with 0·1 N NaOH to screened methyl red. Arsenic, P and Ca do not interfere, but about 95% of the S present as $PbSO_4$ and only about 20% of the S present as $BaSO_4$ is determined. On 32 specimens with a sulphur content of about 40%, the standard deviation of the differences from the Senf and Schöberl method (*Angew. Chem.*, 1937, **50**, 338) was ± 0.076. Encouraging results by this method are reported for sulphosalicylic acid, sulphanilic acid, thiourea and sulphathiazole.
                                    T. R. ANDREW

4368. Rapid method of determining sulphur dioxide in hydrogen fluoride. G. V. Rabovskii, T. N. Egorova and O. P. Kasatkina. *Zavod. Lab.*, 1959, **25** (1), 36–38.—When a saturated soln. of $NaHCO_3$ containing iodine is used as an absorbent for determining SO_2 in gaseous HF the vol. of CO_2 liberated can be used to calculate the vol. of the gas which has been passed into the absorption vessel. The reaction of 1 mole of HF with $NaHCO_3$ yields 1 mole of CO_2, and the reaction of 1 mole of SO_2

with iodine and $NaHCO_3$ yields 4 moles of CO_2. The sample of gaseous HF is passed at a rate of 100 to 150 ml per min. into a vessel containing 100 ml of satd. $NaHCO_3$ soln. together with 1 to 5 ml of 0·01 N iodine and 3 to 5 ml of starch soln. until the absorbing soln. is decolorised. The vol. of CO_2 liberatde is measured by causing it to displace water from an aspirator bottle. The method is applicable to the determination of $\nless 0·01\%$ of SO_2 in gaseous HF with a relative error $\ngtr 7\%$.　　　　　G. S. SMITH

4369. Determination of the sulphur dioxide content of flue gases from boilers. B. A. Chertkov and D. L. Puklina. *Teploenergetika*, 1958, (9), 87–89; *Ref. Zhur., Khim.*, 1959, (3), Abstr. No. 8005.—The iodimetric method of determining SO_2 in flue gases is studied, the determination being carried out in a sample of the gas taken from the total gas flow. Good reproducible results are obtained and the accuracy is within 0·03 mg of SO_2 per litre. A study is also made of the factors influencing the magnitude of the error due to oxidation of the SO_2 to SO_3 by oxygen contained in the gas. To determine the average concn. of SO_2 in flue gas over an interval of time (3 to 40 min.), a method is developed consisting in drawing the sample of gas through a train of absorbers. The use of soln. of iodine or $KClO_3$ is recommended to take up the SO_2; in both cases very precise results are obtained.　　　　　C. D. KOPKIN

4370. Photometric determination of traces of selenium or tellurium in lead or copper. C. L. Luke (Bell Telephone Lab., Inc., Murray Hill, N.J.). *Anal. Chem.*, 1959, **31** (4, Part I), 572–574.—Selenium and Te are isolated from large amounts of Pb or Cu by co-pptn. as the element with As. Selenium is then determined photometrically with 3:4:3′:4′-tetra-aminodiphenyl, and Te is determined as the diethyldithiocarbamate. The recovery of Se is quant., that of Te is $\simeq 93\%$.
　　　　　P. D. PARR-RICHARD

4371. Microgram determination of tellurium by an induced reaction with ferric phenanthroline. C. O. Ingamells and E. B. Sandell (Univ. of Minnesota, Minneapolis, U.S.A.). *Microchem. J.*, 1959, **3** (1), 3–12.—The ferric complex of 1:10-phenanthroline (ferriin) is reduced to the ferrous complex (ferroin) by Te^{IV} in the presence of $K_2Cr_2O_7$, the red colour so produced being measured. *Ferroin soln.* (**I**)—Dissolve 0·05 g of 1:10-phenanthroline-ferrous perchlorate in 50 ml of 0·2% (v/v) H_2SO_4 soln. Allow to stand for several hours before use. The soln. is stable for 2 weeks. *Ferriin soln.* (**II**)—Shake 5 to 10 ml of **I** with 0·1 g of Mn-free PbO_2 till the soln. assumes a pure blue colour. Filter and re-pass the filtrate through the filter to ensure complete oxidation and removal of PbO_2. This soln. is unstable and is prepared immediately before use. HNO_3 *soln.* (1·0 M) (**III**)—Boil conc. HNO_3 for a few minutes to remove oxides of nitrogen. Dilute 20 ml to 300 ml with water and add 1 to 2 mg of urea. For the determination, evaporate the test soln. (containing $\nless 2$ ml of conc. HNO_3 and $\ngtr 25$ μg of Te^{IV}). Dissolve the dry residue in 1 ml of **III** with heating, and dilute to 20 ml with water. Add 1 ml of 1% NaCl soln. (except when Ag is present) followed by 1 ml of **II**, and mix. Add 2 ml of 0·015% $K_2Cr_2O_7$ soln., mix, make up to 25 ml and allow to stand for 10 min. Measure the absorption in a 1- or 2-cm cell at 475 mμ against a blank prepared at the same time with the same batch of **II**, and refer the result to a standard curve. Fixed acids are removed by evaporating the test soln. with

excess of $NaNO_3$. Organic matter that is not completely oxidised by HNO_3 is eliminated by fusion with KNO_3. Interference is strong from Mn^{II}, Cu^{II} and Ce^{III}, less strong with Au, Pd, Rh, Ir, Sn, W and V. No interference occurs with low concn. of Pb, Zn, Th, Hg, Bi, Fe, Mo, Hg, As, K, Na, Ca and Se. The separation of trace amounts of Te from interfering metals is briefly discussed.
　　　　　R. E. ESSERY

4372. Rapid simultaneous potentiometric determination of chromium, vanadium and iron in carbides by means of titanium(III) chloride. O. Dufek and H. Tůma (SVÚMT, Prague). *Hutn. Listy*, 1959, **14** (3), 246–247.—The potentiometric titration of Cr^{VI} to Cr^{III}, V^V to V^{III}, Fe^{III} to Fe^{II} and Mo^{VI} to Mo^V can be carried out in a medium containing $HClO_4$ and HCl. The first potential change corresponds to the reduction of Cr and V^V (to V^{IV}), the second to the reduction of Fe, and the third to that of Mo. After the addition of tartrate or citrate a further step corresponding to the reduction of V^{IV} to V^{III} is observed. The amount of standard soln. consumed in this titration is deducted from that used in the first potential change to determine the amount of $TiCl_3$ corresponding to the Cr. A derivative titration arrangement (platinum and S.C.E. electrodes connected with a galvanometer through a derivation adaptor and sensitivity control) has been found advantageous for the precise determination of potential changes. *Procedure*—Dissolve 10 to 15 mg of the carbide isolated from steel in $HClO_4$ (60%) (3 to 5 ml) and several drops of conc. HNO_3 and evaporate. After 30 min. dilute with several drops of H_2O, add conc. HCl (15 ml) and titrate with $TiCl_3$ soln., while stirring and bubbling with CO_2. After the potential changes corresponding to the reduction of Cr plus V, and Fe plus Mo, add Na citrate soln. (40%) (40 ml) and titrate V^{IV} to V^{III}.　　　　J. ZÝKA

4373. Spectrochemical analysis of super-pure chromium for impurities. C. G. Baird (Defence Standards Lab., Dept. of Supply, Maribyrnong, Victoria, Australia). *Appl. Spectroscopy*, 1959, **13** (2), 29–31.—A method for the determination of Mg, Pb, Fe, Al, Cu and Ag at concn. from 0·0001 to 0·005% is described. The chromium is volatilised as chromyl chloride and the impurities are collected on a $CaSO_4$ matrix, which is then burned in a d.c. arc. Indium is added as an internal standard. At an impurity level of 0·0005% the reproducibility is better than $\pm 0·0001\%$ for Mg, Pb, Fe, Cu and Ag, and is $\pm 0·0002\%$ for Al.　　K. A. PROCTOR

4374. Colour reactions for chromates. I. M. Korenman. *Uch. Zap. Gor'kovsk. Univ.*, 1958, (32), 145–147; *Ref. Zhur., Khim.*, 1959, (1), Abstr. No. 948.—The colour reactions of certain chromotropic acid azo dyes with $Cr_2O_7^{2-}$ in acid medium are studied. Many dyes are very sensitive reagents for $Cr_2O_7^{2-}$, particularly in H_2SO_4, and may be used for its detection. The most sensitive reaction is with 2-(4-dimethylaminophenylazo)chromotropic acid, with a limiting dilution of 1 in 4×10^5; no interference is caused by the presence of Al, Zn, Cd, Hg, Bi, Cu, Ag, Co, Ni, Mn, or alkali or alkaline-earth metals. Other oxidising agents (MnO_4^-, Fe^{3+}) also cause a change in colour of the dyes studied, but the sensitivity of these reactions is less than with $Cr_2O_7^{2-}$. The ability of various oxidants to react analogously to $Cr_2O_7^{2-}$ is a basis for considering the change of colour of the dyes as being due to their oxidation.　　　　C. D. KOPKIN

4375. Photometric determination of molybdenum with ferrocyanide. L. T. Krasivskaya and R. P. Vorontsov. *Trudÿ Ural'sk. Lesotekhn. Inst.*, 1958, (12), 33–38; *Ref. Zhur., Khim.*, 1959, (3), Abstr. No. 7990.—The intensity of the colour of colloidal soln. of molybdenum^{VI} ferrocyanide in acid media obeys Beer's law for concn. of Mo of 0·004 to 0·13 mg per ml, but the soln. are stable for only 5 or 10 min. The colour intensity depends on the acid concn. and is a max. in 0·15 N HCl. On this basis a colorimetric method for determining Mo is developed. The dissolution of the sample and the separation of Mo as the sulphide is carried out in the normal way. Make the soln. up to 100 ml, take a 5 to 20-ml aliquot so that the final concn. of Mo will be $\simeq$0·03 mg per ml, dilute with water, add 0·7 ml of HCl (1 : 1) and 1 ml of 0·1 N $K_4Fe(CN)_8$ and dilute to 30 ml. Measure the extinction within 30 min. of adding the ferrocyanide, with a blue filter. With a path length of 20 mm and a concn. of Mo $\simeq$0·03 mg per ml, the error is 0·002 to 0·004%. With a path length of 50 mm, $<$0·002 mg of Mo per ml may be determined. The described method is 5 times as sensitive as the thiocyanate method.

C. D. KOPKIN

4376. Separation of molybdenum from vanadium by extraction as tributylammonium molybdate thioglycollate. M. Ziegler and H.-G. Horn (Inorg. Chem. Inst., Univ., Göttingen, Germany). *Z. anal. Chem.*, 1959, **166** (5), 362–364.—After complexing the Mo and V with thioglycollic acid and tributylammonium chloride, the molybdenum complex is extracted with dichloromethane at pH 2, the dichloromethane is evaporated and after wet oxidation of the residue with 6 ml of conc. HNO_3 and 1 ml of HCl the Mo is pptd. with $Pb(NO_3)_2$ in the presence of 50 ml of 50% ammonium acetate. The $PbMoO_4$ is filtered off, washed with 2% NH_4NO_3 soln. and H_2O and then dried at 500° to 600°. The average error is 0·4%.

B. B. BAUMINGER

4377. Turbidimetric determination of traces of phosphorus in tungsten and other metals. A. J. Hegedüs and M. Dvorszky (Forschungsinst. f. d. nachrichtentech. Ind., Tungsram, Budapest, Hungary). *Mikrochim. Acta*, 1959, (2), 202–209 (in German).—*Procedure*—The sample (1 g of WO_3) is dissolved in 10 ml of H_2O containing 0·6 g of Na_2CO_3 by warming. The cooled soln. is neutralised with HCl to phenolphthalein, and the following reagents are added in the order indicated—10 ml of aq. NH_3 (10%), 2 g of NH_4Cl, 10 ml of Na_2AsO_4 soln. (containing 3 mg of As per ml) and 10 ml of $MgCl_2$ soln. (10% in 5% NH_4Cl) dropwise with constant stirring. The mixture is diluted with H_2O to 50 ml and set aside for several hours. The ppt. is filtered off on a G4 filter, washed with 5 ml of aq. NH_3 (1%) and dissolved in 20% HCl (using a total vol. of 20 ml). To the soln. are added 5 ml of formic acid (80%) and 5 ml of HBr (24%) and the mixture is evaporated by using an i.r. lamp. The dissolution in HCl and treatment with formic acid and HBr are repeated. Finally, 0·5 ml of conc. HNO_3 is added to the residue and evaporated to destroy HBr; the residue is dissolved in 3·7 ml of HNO_3 (8 N) and washed into a 25-ml flask with a little H_2O and the flask is immersed in a water bath at 20°. After 15 min., 2·5 ml of strychnine - molybdic acid soln. (specified) at 20° is added, the mixture is made up to vol. with H_2O, shaken, replaced in the water bath for 1 hr. and the extinction measured at 530 mμ; 5×10^{-5} % of P can be determined in 1 g. The determination of traces of

P in copper, silver, magnesium, chromium, molybdenum, manganese, cobalt, nickel, aluminium, silicon and germanium is discussed.

B. B. BAUMINGER

4378. Flame-photometric micro-determination of traces of sodium, potassium and calcium in tungsten metal and tungsten oxide. A. J. Hegedüs, J. Neugebauer and M. Dvorszky (Forschungsinst. f. d. nachrichtentech. Ind., Tungsram, Budapest, Hungary). *Mikrochim. Acta*, 1959, (2), 282–293 (in German).—With the apparatus described and illustrated, W is volatilised by means of air saturated with CCl_4 at 450° to 600° and separated from alkali and alkaline-earth metals, which are then determined in the residue with a flame photometer. The completeness of the separation depends on the purity of the W or WO_3. The choice of boat in which the sample is volatilised is of importance, and it is shown that quartz boats are satisfactory, whereas platinum boats give low recoveries of Na. Gold, silver and molybdenum boats were unsatisfactory. The individual methods for the determination of traces of K, Na and Ca are discussed and the results tabulated.   B. B. BAUMINGER

4379. Dissolution of uranium metal and its alloys. R. P. Larsen (Chem. Engng Div., Argonne Nat. Lab., Lemont, Ill.). *Anal. Chem.*, 1959, **31** (4, Part I), 545–549.—The general dissolution characteristics of U are described and methods for dissolving the metal and its alloys are reviewed. The following solvents are considered—HNO_3, HCl, aqua regia, $HClO_4$, H_2SO_4, HF, H_3PO_4, heavy-metal salts, ethyl acetate with Br or HCl and NaOH - H_2O_2. A table of common uranium alloys and their appropriate solvents is given; the choice of solvent depends to some extent on the subsequent determinations to be performed on the soln.

P. D. PARR-RICHARD

4380. New spectrophotometric method for the determination of uranium. F. da Silva and L. de Moura (Comissão de Estudos da Energia Nuclear, Lisbon). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/1814, 17 pp.—Small amounts of U_3O_8 are determined by making use of the displacement of the lactone form of Rhodamine B (C.I. Basic Violet 10) to the quinone form by the action of uranyl salts of carboxylic acids sol. in benzene. The colour is determined spectrophotometrically; Beer's law is obeyed for 5 to 80 μg of U_3O_8 per ml. The best operating conditions are selected and the main sources of interference considered; these are Fe, Sn, Mn, Sb and Tl. Since Cu and Al do not interfere, the classical scheme of separation may be followed. Some results for minerals poor in uranium are shown in comparison with those obtained by other methods.

NUCL. SCI. ABSTR.

4381. Isotopic analysis of uranium by emission spectroscopy. G. V. Wheeler (Phillips Petroleum Co., Atomic Energy Div., Idaho Falls). Conf.: "Modern Approaches to the Isotopic Analysis of Uranium." Chicago, Feb. 5–7, 1957. Rep. TID-7531(Pt.2)(Del.), 25–31.—The isotopic analysis of U by emission spectroscopy has been investigated at the Idaho Chemical Processing Plant in three phases; a literature search, an investigation with the equipment available at the Idaho Chemical Processing Plant, and an investigation with high-resolution direct-reading equipment available commercially. These investigations are discussed and the conclusion is drawn that though more work

remains to be done, U can be assayed for ^{233}U, ^{235}U, ^{236}U and ^{238}U by emission spectroscopy with a precision approaching that of mass spectrometers but at much lower cost.   NUCL. SCI. ABSTR.

4382. Isotopic analysis of uranium by the emission spectrograph. R. E. Kupel and W. Tichy (General Electric Co., Aircraft Nuclear Propulsion Dept., Cincinnati, Ohio). Conf.: "Modern Approaches to the Isotopic Analysis of Uranium." Chicago, Feb. 5–7, 1957. Rep. TID-7531(Pt.2)(Del.), 17–24.—The method is suitable for the analysis of U in the 90% enrichment range. Two graphite electrodes are loaded with an equal mixture of graphite and U and excited in an a.c. arc. The resulting spectra are monitored on a densitometer to obtain the relative intensities of the 4244·37-A line and the 4261·51-A line. The ratio of the relative intensities of these two lines is then applied to a concn. curve and the percentage of ^{235}U is obtained from the curve. A known amount of material is weighed and dissolved in HNO$_3$. A measured volume of soln. is evaporated on a stainless-steel disc and the α-activity is obtained with a proportional counter. The ^{234}U (%) is calculated from the α-activity, the ^{236}U (%) is obtained as described above, and the ^{235}U (%) is then obtained by difference, assuming that only the three isotopes are present. The accuracy of this method compares favourably with the mass-spectrometer method. The precision of the method at the 95% confidence level is $\pm 0\cdot30\%$.   NUCL. SCI. ABSTR.

4383. Uranium-235 abundance by γ-spectrometry. S. A. Reynolds and J. S. Eldridge (Oak Ridge National Lab., Tenn.). Conf.: "Modern Approaches to the Isotopic Analysis of Uranium." Chicago, Feb. 5–7, 1957. Rep. TID-7531(Pt.2)(Del.), 47–52.—Techniques are described for determining ^{235}U abundance by measurement of the intensity of 0·18-MeV γ-radiation. One method involves the measurement of the ratio of the intensity of 0·18-MeV radiation to that of $\simeq 0\cdot1$-MeV radiation. The preferred technique consists in the chemical separation of U, followed by direct counting of the 0·18-MeV photons. Application has been made in analysis of U samples of abundances in the range of 0·05% to 93%. The accuracy appears to be better than 3% if the abundance is between 0·7% and 100%. Data in the self-absorption of 0·18-MeV radiation in uranium oxide are presented.   NUCL. SCI. ABSTR.

4384. A γ-counting method for the determination of uranium-235 in enriched uranium. U. L. Upson and D. G. Miller (General Electric Co., Hanford Atomic Products Operation, Richland, Wash.). Conf.: "Modern Approaches to the Isotopic Analysis of Uranium." Chicago, Feb. 5–7, 1957. Rep. TID-7531(Pt.2)(Del.), 32–46.—The ^{235}U can be detected and measured in the presence of other U isotopes and their daughters by selectively measuring its 184-keV γ-radiation. The determination of the ^{235}U content of highly enriched uranium in aluminium alloys is described. In this case it is possible to do the counting on small vol. of dissolved samples of the alloy without separation of the aluminium or of the uranium daughters. A precision of $\pm 1\cdot2\%$, at the 95% confidence level, is possible by the technique described. The effects of daughter growth and of separation of the U from the Al are discussed, as well as other methods for improving the precision.   NUCL. SCI. ABSTR.

4385. Radiochemical method for the determination of uranium in rocks by means of fractional extraction

of thorium-234 with hexone [*isobutyl* methyl ketone]. G. Alberti, C. Bettinali, F. Salvetti and S. Santoli (Chem. Lab., Geomineral. Div., C.N.R.N., Inst. of Gen. and Inorg. Chem., Univ. of Rome). *Ann. Chim., Roma,* 1959, **49** (1), 199–204.—Uranium-238 is in equilibrium with its direct radioactive decay product, ^{234}Th, which in turn establishes an equilibrium with ^{234}Pa within $\simeq 5$ min. To ascertain the uranium content of rocks, the ^{234}Th is separated from interfering radio-elements by preferential extraction with *iso*butyl methyl ketone and the β-emission of the ^{234}Pa is counted. The results are then compared with those obtained by similarly treating standard soln. of uranyl nitrate. The method is rapid and is suitable for concn. of U as low as 0·005%. No interference is shown by isotopes of Pb and Bi, or by PO$_4{}^{3-}$, SO$_4{}^{2-}$ and Cl⁻.
          A. G. COOPER

4386. Direct measurement of uranium and thorium by γ-spectroscopy. C. Brooke, E. Picciotto and G. Poulaert (Univ. Libre, Brussels). *Bull. Soc. Belge Géol. Paléontol. Hydrol.,* 1958, **67** (2), 315–328 (in French).—The development of spectrometric methods for determining U and Th and the usefulness of the techniques in geochemical and geochronological research are discussed. Experiments are described in which Th and U are determined simultaneously in weighed artificial mixtures by γ-spectroscopy. The error increased when the concn. decreased and also increased when the U to Th ratio differed from 1. The error ranged from 1% for concn. near 0·1 g per g to 10% for concn. of several mg per g. To maintain the error in Th and U determination at less than 10%, the U to Th ratio should be between 0·1 and 10. For source densities of about 0·2 g per cu. cm the determination is not affected by variations in the density or nature of the sample. The determination can be made in 30 min. directly on a powder of the mineral or rock.   NUCL. SCI. ABSTR.

4387. Analysis of uranium, thorium and zirconium. G. Almássy, M. Ördögh and A. Schneer (Central Res. Inst. for Physics, Budapest). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/1718, 18 pp.—In investigating the physico-chemical conditions for the tributyl phosphate extraction of U, the optimum concn. of NO$_3$⁻ in the aq. phase in which the separation of U by single extraction amounted virtually to 100% was determined. The extraction was carried out in tributyl phosphate - kerosine and the U re-extracted in dil. ammonium carbonate soln. The U content was determined by the reduction of U^{VI} to U^{IV} and subsequent oxidising with Fe^{III}, which can be measured by the light absorption of the 2:2′-dipyridyl complex equiv. to U at 500 mμ. For the chromatography of Th it has been found that, with the solvents indicated in the literature, the Th produces an elongated spot on a cellulose column or on paper. This spot becomes more compact by increasing the acid and water content of the solvent. The optimum composition of the solvent was determined: 8 N HNO$_3$ was shaken with an equal amount of diethyl ether and after separation of the two phases the ether phase was used. Among the colorimetric determinations of Th, the thoron method was improved for the analysis of ores by reducing Fe^{III} with ascorbic acid. The sensitivity of the method is increased by $\simeq 70\%$ by the addition of methanol. Zirconium and hafnium can be separated selectively by mandelic acid. The ppt., containing 0·2 to 3 mg of Zr, is dissolved in excess

of conc. H_2SO_4 and the mandelic acid, bound quant. to the Zr can be oxidised to CO_2 and water with $Na_2Cr_2O_7$ soln. In the presence of 2 to 20 mg of Zr, the oxidation can be carried out in excess of $KMnO_4$ soln. in a fairly alkaline medium. The vivid yellow zirconium - morin complex, which shows a green fluorescence in u.v. light, is suitable for the photometric determination of Zr. Measurements can be carried out between 420 and 470 mμ.

NUCL. SCI. ABSTR.

4388. Use of radioactive isotopes in studying the spatial distribution of elements in direct current arc plasma during spectrochemical determination of impurities in uranium. É. E. Vaĭnshteĭn and Yu. I. Belyaev (V. I. Vernadsky Inst. of Geochem. and Anal. Chem., Acad. of Sci., Moscow). *Intern. J. Appl. Radiation and Isotopes,* 1959, **4** (3–4), 179–188.—Uranium oxide with various added compounds labelled with γ-active nuclides was examined spectrographically. In addition to normal photographing of the discharge, the distribution of the added element was determined by observation of the γ-activity with a pin-hole camera. The distributions of Sb, Ga and Cu in various proportions were studied particularly from the aspect of the use of Ga_2O_3 as a carrier in the determination of Sb; the distributions of Ag, and of Na, Ca and Ga were also examined. It was concluded that, (*i*) the distribution of an element depends upon its volatility, (*ii*) the distribution of a micro-constituent follows that of a macro-constituent when both constituents are being removed from a base of low volatility, and (*iii*) the materials used as carriers contain elements that are symmetrically distributed in an arc between the electrodes.

G. J. HUNTER

4389. Separation of traces of rare-earth elements in uranium by ion exchange. H. A. Braier (Comisión Nacional de Energía Atómica, Buenos Aires). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/1568 (Rev.1), 8 pp.— A soln. of UO_2^{2+}, with traces of Eu, in a H_2SO_4 medium is passed through a bed of cationic resin, so that the anionic complex of the UO_2^{2+} passes through and the rare-earth elements are retained. The remainder of the U is eluted with H_2SO_4, and the rare-earth elements are eluted with HCl. The final determination is made spectrographically. The fixation of Eu by the resin and its subsequent elution is observed by adding [154]Eu, which acts as a tracer. This method is promising for the determination of the rare-earth elements in uranium because it is simpler than those described in the literature.

NUCL. SCI. ABSTR.

4390. Determination of isotopic ratios in uranium hexafluoride using dual ionisation chambers. J. H. Lykins, E. C. Denny and W. G. Schwab (Oak Ridge Gaseous Diffusion Plant, Tenn.). Conf.: "Modern Approaches to the Isotopic Analysis of Uranium." Chicago, February 5–7, 1957. Rep. TID-7531-(Pt.2)(Del.), 7–16.—A dual ionisation chamber method was investigated for possible use in determining small differences in [235]U concn. in uranium hexafluoride. Two ionisation chambers are connected in ion polarity opposition, and the differential ion current is collected on a capacitor. Instrumentation automatically converts the information to digital form and records the time required to collect a fixed charge. Also studied was an alternative method of measuring the ratios of times required for the voltage to change by a fixed interval.

NUCL. SCI. ABSTR.

4391. A new electrolytic carrier for the determination of uranyl ion. C. J. Sambucetti and A. Gori (Comisión Nacional de Energía Atómica, Buenos Aires). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/1576, 25 pp.—The polarographic behaviour of the complex formed between UO_2^{2+} and tiron (disodium catechol-3:5-disulphonate) is reviewed, and the best conditions for the determination of the U present in this medium are established. The electrode reaction is reversible in the pH range from 2 to 3·5. The $E_{\frac{1}{2}}$ varies with the pH; its values range from 0·222 to 0·243 V (*vs.* the S.C.E.), with a tiron concn. of 0·05 M. The possible electrode reaction is indicated.

NUCL. SCI. ABSTR.

4392. Spectrophotometric determination of contamination in nuclearly pure uranyl nitrate. J. Nowicka-Jankowska, A. Gołkowska, I. Pietrzak and W. Zmijewska (Polish Acad. Sci., Inst. Nucl. Res., Warsaw). Inst. of Nucl. Res., Warsaw, Rep. No. 45/VIII, 1958, 42 pp.—Methods of determining trace amounts of Ni, Al, Si, Mo, Cr and Fe in uranyl nitrate are described. Nickel is determined with dimethylglyoxime, Al with haematoxylin and Si as molybdenum blue. Molybdenum may be determined by the thiocyanate method, or with dithiol, Cr is determined with diphenylcarbazide, and Fe with 2:2′-dipyridyl. NUCL. SCI. ABSTR.

4393. Improved method for the determination of trace quantities of plutonium in water. J. Kooi, U. Hollstein and M. Schlechter (Reactor Centrum Nederland, The Hague). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/550, 18 pp.—The method is based on the extraction of the cupferron complex following a concentration step. It was found that bismuth phosphate may advantageously be used as the co-pptg. agent. Measurements of the extraction, with $CHCl_3$, of Bi, Fe and Pu as cupferrates were performed. By properly adjusting the pH, a good separation of Bi and Pu may be achieved. A substantial reduction in the amount of Fe was found to be possible, reducing sample-size and self-absorption losses in α-counting. The yield of Pu compares favourably with that obtained by other methods.

NUCL. SCI. ABSTR.

4394. Analysis for neptunium-237 in nitric acid solutions. B. B. Murray (E. I. du Pont de Nemours & Co., Savannah River Lab., Augusta, Ga.). *U.S. Atomic Energy Comm.,* Rep. DP-316, 1958, 14 pp.—A method was developed for the determination of [237]Np in HNO_3 soln. that contained U, Pu and fission products. Neptunium was extracted with 2-thenoyltrifluoroacetone after reduction to the quadrivalent state with ferrous sulphamate. The α-activity of the separated Np was then measured with an α pulse height analyser, and the degree of separation of Np from other α-emitters was determined. The precision of the analysis depended on the total amount of [237]Np present in the sample. A coeff. of variation of 2 to 5% was observed for samples that contained more than 180 α-disintegrations of Np per min. For activities in the range of 10 disintegrations per min., the coeff. of variation was from 10 to 25%. NUCL. SCI. ABSTR.

4395. Microcrystalloscopic reactions for halogens using organomercury compounds. I. M. Korenman and A. A. Belyakov. *Uch. Zap. Gor'kovsk. Univ.,* 1958, (32), 85–91; *Ref. Zhur., Khim.,* 1959, (1),

Abstr. No. 975.—The microcrystalloscopic reactions of Cl⁻, Br⁻ and I⁻ with 23 mono- and di-mercurated compounds of aniline and its derivatives, toluidines, quinoline and 2-aminopyridine are studied. Several of these compounds show sensitive and specific reactions with the halides, the most sensitive being the mono-mercury compounds. The sensitivity increases from Cl⁻ to I⁻, while the max. crystal size decreases. Many of the crystalline ppt. show intense pleochroism.   C. D. KOPKIN

4396. Emission spectrographic analysis of fluorine with reference to the calcium fluoride band. V. R. Ognev. *Trudy Sibirsk. Fiz.-Tekh. Inst., Tomsk. Univ.*, 1958, (36), 281–286; *Ref. Zhur., Khim.*, 1959, (9), Abstr. No. 31,048.—Fluorine is determined in bone and in materials the basic components of which are SiO_2 or NaCl. *Procedure*—Mix the sample with CaO (1:1) and excite the spectra in an a.c. arc between two carbon electrodes arranged at an angle of 90° in a horizontal plane. Calibration curves are constructed with the bands CaF (5291 A) and CaO (5473 A). The probable error is ± 6%. In the presence of large amounts of Ca the sample need not be mixed with CaO.
                                            K. R. C.

4397. Determination of fluorine in beryllium compounds. J. L. Huguet (Comisión Nacional de Energía Atómica, Buenos Aires). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/1582, 10 pp.—The applicability of titrimetric methods to the micro- and macro-determination of F in beryllium compounds was studied. A study is presented of the effect of various factors on the separation of F by distillation, and a technique is designed which affords means of obtaining distillates having characteristics compatible with the application of the titrimetric methods.
                                  NUCL. SCI. ABSTR.

4398. Rapid determination of fluorine, sulphur, chlorine and bromine in catalysts with an induction furnace. A. L. Conrad, J. K. Evans and V. F. Gaylor [Chem. and Phys. Res. Div., The Standard Oil Co. (Ohio), 4440 Warrensville Center Rd., Cleveland, Ohio]. *Anal. Chem.*, 1959, **31** (3), 422–425.—Rapid combustion methods are described for determination of F, S and Cl, and S and Br. Fluorine is volatilised as fluorosilicic acid in the presence of silica gel and an accelerator (iron) and absorbed in dil. NaOH soln. (pH 9 to 9·5); F⁻ are then titrated with $Th(NO_3)_4$ soln. at pH ≈3, with Na alizarinsulphonate as indicator; the end-point is found spectrophotometrically at 520 mμ. To determine S and Cl, the Cl is absorbed in aq. 0·005 N $AgNO_3$ at pH 1 and the excess of Ag is titrated amperometrically; S, which is not retained by 0·005 N $AgNO_3$, is titrated continuously, as it is evolved, by KIO_3 soln. For the determination of S and Br, the Br is absorbed in cold CCl_4, extracted with ice-water and titrated with $Na_2S_2O_3$ soln. after addition of KI and H_2SO_4; S is determined as before.
                                  P. D. PARR-RICHARD

4399. Micro-method for determining fluorine monoxide. E. A. Peregud and B. S. Boĭkina (State Scientific-Res. Inst. of Work Hygiene and Occupational Diseases, Leningrad). *Zhur. Anal. Khim.*, 1959, **14** (1), 141–142.—Microgram amounts of F_2O in air are determined by drawing 1 litre of the air in 20 min. through an indicator tube containing silica gel moistened with a soln. of fluorescein containing KBr and K_2CO_3 (*cf. Zhur. Anal. Khim.*, 1957, **12**,

513); F_2O liberates Br from the KBr, with the subsequent formation of the red tetrabromofluorescein. The length of the coloured zone is proportional to the concn. of F_2O.
                                            C. D. KOPKIN

4400. Determination of chloride in uranium-bearing materials by a potentiometric titration method. P. G. Laux and E. A. Brown (National Lead Co. of Ohio, Cincinnati). *U.S. Atomic Energy Comm.*, Rep. NLCO-751, 1958, 39 pp.—The method is suitable for the determination of Cl⁻ in the range of 0·005 to 0·15% in uranium-bearing feed materials. The titration is carried out to a predetermined equivalence potential in a methanol - HNO_3 (19:1) medium. A silver wire - saturated calomel electrode system is used. The method is rapid since no preliminary separation of the Cl⁻ is required. The major interferences are caused by Fe^{III}, V^V, MnO_4^-, NO_3^-, Br⁻ and I⁻. The interference of all ions except Br⁻ and I⁻ is prevented by the addition of ascorbic acid or aq. NH_3. A comparative study of the potentiometric and turbidimetric methods was made. Uranium ore concentrates, HNO_3 and aq. feed samples were used in this study. Satisfactory agreement was obtained between the two methods.   NUCL. SCI. ABSTR.

4401. Iodimetric assays. VI. The determination of iodide ions in the presence of bromide and chloride. L. Szekeres and E. Kardos. *Magyar Kém. Lapja*, 1958, **13** (10–12), 447.—Iodide is oxidised with Cl or BrO⁻ and the excess of oxidant is selectively reduced with H_2O_2, Na formate, Na oxalate, urea or ethanol; IO_3^- are then determined iodimetrically. *Procedure*—To a sample of 0·01 to 0·025 N KI (5 to 10 ml) add approx. 0·1 N KBr - Br (10 to 25 ml) and $NaHCO_3$ (3 to 5 g) and dilute with a few ml of H_2O. After 1 to 2 min. add ethanol (5 to 15 ml) and heat for 15 min. on a water bath. Dilute the soln. to 100 ml, acidify with 10 N HCl (10 ml) and titrate the iodine with 0·02 to 0·1 N $Na_2S_2O_3$. The presence of Br⁻ or Cl⁻ has no effect on the result. The error is < 0·7%.   G. SZABO

4402. X-ray fluorescence method for determining iodide in photographic processing solutions. Iodide concentration technique. D. Owerbach, R. F. Hoefler and H. J. Klem (Colour Technol. Div., Eastman Kodak Co., Rochester, N.Y., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 579–581.—By this method concn. of iodide as low as 1 mg per litre can be determined with a coeff. of variation of ≈ ± 4%. The iodide is pptd. with a slight excess of $AgNO_3$, filtered off and dried, and the ppt. is analysed against a known standard. The effects of varying concn. of bromide at different iodide levels have been studied and some possible interferences in the X-ray technique are discussed.
                                            K. A. PROCTOR

4403. New reagents for the detection of technetium. F. Jasim, R. J. Magee and C. L. Wilson (Dept. of Anal. Chem., Queen's Univ., Belfast). *Talanta*, 1959, **2** (1), 93–95.—Four colorimetric reagents for technetium are described. *Procedure with potassium ethylxanthate*—To 10 mμl of the test soln. add 50 mμl of satd. aq. potassium ethylxanthate soln. and 50 mμl of 2 N HCl. The presence of Tc^{IV} or Tc^{VII} is indicated by the immediate formation of a purple colour, which is readily extractable into CCl_4. The limit of identification is 0·02 μg of Tc; Mo interferes. *Dimethylglyoxime and $SnCl_2$*—To 100 mμl of the test soln. add 100 mμl of satd. dimethylglyoxime soln. in 95%

ethanol and 50 mμl of SnCl$_2$ soln. (15 to 30% in 10 N HCl). A green colour indicates the presence of Tc^{IV} or Tc^{VII}. The limit of identification is 0·04 μg. *Thiourea*—To 100 mμl of the test soln. add 50 mμl of 2 N HNO$_3$ and 50 mμl of 10% aq. thiourea soln. An orange - red colour confirms the presence of Tc. The limit of detection is 0·04 μg. *KSCN in HCl*—To 100 mμl of the test soln. add 50 mμl of 6 N HCl and 40 mμl of aq. KSCN soln. (20%). Heat in boiling water for 5 min. A purple colour confirms the presence of Tc^{IV}.

W. T. CARTER

4404. Separation of technetium from rhenium by paper electrophoresis. R. A. Guedes de Carvalho (Comissão de Estudos da Energia Nuclear, Oporto, Portugal). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/1810, 5 pp.—The separation is achieved by reduction of Tc^{VII} to Tc^{IV}, which is cationic or does not migrate, while Re^{VII} is not affected by the reductant and maintains its anionic character. Among several reductants studied, buffered soln. of hydrazine hydrate and sulphate (pH = 8 to 9) and hydriodic acid permitted very good and rapid separations of the two elements.

NUCL. SCI. ABSTR.

4405. Separation of iron from certain metals by ion-exchange chromatography. R. N. Golovatyĭ. *Ukr. Khim. Zhur.*, 1958, **24** (3), 379–383; *Ref. Zhur., Khim.*, 1959, (1), Abstr. No. 896.—The described method for separating Fe^{3+} from Ca, Mg, Ba, Mn, Co, Ni, Cu, Ti, Zn and Al is based on the formation of a stable anionic complex of Fe^{3+} which is not adsorbed by a cationite in the H form. Add EDTA (disodium salt) (**I**) as the complexing reagent from a burette, determining the moment of completion of the complexing of Fe by the change in colour of the soln. containing KSCN or sulpho-salicylic acid. To separate Fe from Al, Mg, Ba, Mn, Cu and Ni, acidify the soln. to 0·01 N with HCl, add 4 or 5 drops of 10% KSCN soln., and then 0·1 N **I** till the thiocyanate complex is decolorised. Pass the resulting soln. through a column of diam. 1·2 cm containing 10 g of Wofatit (H form) at a rate of 3 to 4 ml per min. All the cations except Fe^{3+} are adsorbed by the resin. Elute the adsorbed ions with 3 N HCl. The described method can be used for the separation of Fe from Co if the pH of the soln. is first adjusted to $\not> 2$. Elute Co with 3 N HCl and determine it by the method described earlier [Pribil, *"Kompleksonÿ v Khimicheskom Analize"*, Izd. Inostr. Lit., 1955, pp. 86, 94]. To separate Fe^{3+} and Cr^{3+} from Ti^{4+}, add **I** to the soln. until Fe and Cr are bound in a stable complex not destroyed by cationites at pH 1 to 10, heat the soln. to between 40° and 60°, cool, and pass the soln. through a column of cationite. Elute the adsorbed Ti with warm 2 N H$_2$SO$_4$ containing 1% of oxalic acid, oxidise the oxalic acid with permanganate, and determine Ti photometrically. C. D. KOPKIN

4406. Determination of various forms of iron in rocks. Yu. P. Trusov (V. I. Vernadskiĭ Inst. of Geochem. and Anal. Chem., Acad. of Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (1), 139–140. —Ferrous, ferric and pyritic Fe are determined in a single sample by heating the coarsely ground sample (0·5 or 1 g) in a stream of CO$_2$ with a mixture of 20 ml of H$_2$SO$_4$ (1 : 2) and 10 ml of HF, cooling, pouring the mixture into about 80 ml of satd. H$_3$BO$_3$ soln., and titrating with 0·1 N KMnO$_4$ to determine Fe^{2+}; Fe^{2+} plus Fe^{3+} is determined by filtering off the pyrites (which is not attacked by this

treatment), washing it with water, adding to the filtrate 15 ml of 25% NH$_4$SCN soln. and titrating the Fe with 0·1 N Hg$_2$(NO$_3$)$_2$; Fe^{3+} are found by difference. The residue of pyrites is ignited at about 800°, the Fe$_2$O$_3$ is fused with K$_2$S$_2$O$_7$, the melt dissolved by heating with H$_2$SO$_4$ (1 : 20), and Fe^{3+} are titrated with Hg$_2$(NO$_3$)$_2$. The method may be used for rocks not containing considerable amounts of oxidising - reducing substances.

C. D. KOPKIN

4407. Quantitative spectrographic analysis of ferrotitanium. A. A. Tsimbal and V. Lichko. *Sudostroenie*, 1958, (7), 67–68; *Ref. Zhur., Khim.*, 1959, (2), Abstr. No. 4362.—Grind an average sample (20 g) and sieve. Mix 1 g of sample and 1 g of copper powder and press into a briquette with a pressure of 4000 kg per sq. cm, and clamp the briquette opposite a carbon electrode. Excite the spectra in a high-voltage spark discharge (circuit capacity 0·01 μF, self-induction zero, discharge gap 3 mm, and working gap 2 mm), and photograph in a medium spectrograph with an exposure of 100 sec. and a preliminary ignition of 30 sec. Construct calibration curves from the lines (in A)—Ti 3653·4 and Fe 3631·4, Si 2881·5 and Fe 2872·3, and Al 2816·1 and Fe 2831·5. To determine Cu, use a briquette prepared from 1 g of sample and 1 g of Al, and analytical lines Cu 3273·9 A and Ti 3653·4 A. The analytical error is $\not> 2·0\%$. C. D. KOPKIN

4408. Electrolytic isolation of non-ferrous inclusions in steel with the use of a modified Klinger and Koch apparatus. L. Brháček, J. Janáček and A. Šmrhová (Res. Inst. VŽKG, Ostrava, Czechoslovakia). *Hutn. Listy*, 1959, **14** (1), 54–55.—A modification of the Klinger and Koch apparatus (*Arch. Eisenhüttenw.*, 1938, **11**, 569) permits shortening of the time required for the isolation of inclusions by means of the high current density of 0·10 amp. per sq. cm. A detailed description of the apparatus and procedure is given. For samples with surface areas of 30 to 50 sq. cm, a current of 1 to 2 amp. and an electrolysis time of 24 hr. are recommended. A suitable anolyte is Na citrate (40 g), citric acid (10·5 g), KBr (15 g), NaCl (20 g) and KI (1 g) in 1 litre of H$_2$O, and a suitable catholyte is citric acid (86 g) and N Na$_2$CO$_3$ (1 ml) in 1 litre of H$_2$O; 500 ml of electrolyte is recommended per g of dissolved sample.

J. ZÝKA

4409. Determination of copper in steel by amperometric titration with sodium diethyldithiocarbamate. Yu. I. Usatenko and F. M. Tulyupa (F. É. Dzerzhinskiĭ Dniepropetrovsk Chem. Tech. Inst.). *Zavod. Lab.*, 1959, **25** (3), 280–283.—The sample (1 g) is heated with 20 to 30 ml of dil. HCl (1 : 1), and the soln. boiled with 2 to 3 ml of conc. HNO$_3$ (5 ml if W is present); 25 to 30 ml of water is added, and the soln. is boiled to remove oxides of N, and Cl, then neutralised with aq. NH$_3$ and HNO$_3$, cooled, and diluted to 100 ml. An aliquot (10 ml) is mixed with 2 ml of 0·1 M Pb(NO$_3$)$_2$ (to serve as an indicator), 0·5 g of K tartrate (neutral or acid salt) and 1 g of Na acetate. If a white cloudiness (Pb tartrate) does not appear a further amount of Na acetate is added. A few drops of satd. NH$_4$Cl soln. are added to dissolve the ppt. and the soln., after being diluted to 50 ml, is titrated amperometrically with 0·2% Na diethyldithiocarbamate soln. at an applied potential of +0·8 V vs. the S.C.E. at a rotating platinum electrode. When W is present the WO$_3$ is filtered off and washed with

very dil. HCl soln. before the neutralisation with aq. NH_3. The tartrate present prevents interference by Cr and Mn. Large amounts of Ni, Mo and V do not interfere.   G. S. SMITH

4410. Determination of copper in certain high-alloy steels. C. R. Elliott, P. F. Preston and J. H. Thompson (Materials Sect., Test & Inspection Branch, P.O. Engng Dept., Fordrough Lane, Birmingham, England). *Analyst*, 1959, **84**, 237–239.—The sample is dissolved in dil. H_2SO_4 (or with stainless steel in dil. H_2SO_4 with subsequent oxidation of residual carbides with HNO_3), the liquid is heated to fuming, diluted to a known vol. and an aliquot, suitably diluted, is extracted with 0·5% dithizone soln. and finally with CCl_4 to remove residual dithizone. The combined extracts are heated with a mixture of H_2SO_4, HNO_3 and $HClO_4$ to oxidise organic matter. Citric acid soln. is added, the pH is adjusted to 8 to 9·5 with aq. NH_3, and the liquid is treated with 0·5% bis*cyclo*hexanone oxalyldihydrazone soln. in 50% ethanol (5 ml) at 20°. After development of the colour the liquid is diluted to vol., and its extinction is measured at 595 mμ against water, and referred to a calibration graph prepared from a standard soln. (1 mg of Cu per 10 ml). The most useful range of Cu in the final soln. is $\simeq$ 40 to 200 μg per 100 ml. The precision is satisfactory.   A. O. JONES

4411. Porous cup technique in the determination of magnesium in cast iron. A statistical study. A. C. Ottolini (General Motors Corp., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1959, **31** (3), 447–449.—Chemical methods for the determination of Mg in cast iron are lengthy and inaccurate. The spectrographic method described is rapid and the coeff. of variation (95 tests) was $\pm 1\cdot83\%$. A graphite porous cup was used as the sample electrode, and synthetic standards containing Fe and Mg were used to establish the analytical curve. A series of tests established instrument repeatability, chemical errors due to sample preparation, day-to-day reproducibility, and total over-all deviation.

P. D. PARR-RICHARD

4412. Spectrographic analysis of small amounts of rare-earth elements in alloy steel. Shüh-Cho Li and Yü-Me Wang (Inst. of Metal Res., Acad. Sinica). *Acta Metallurg. Sinica*, 1959, **4** (1), 81–86.—In the method employed (*cf.* Spitz *et al.*, *Anal. Abstr.*, 1954, **1**, 1221), either the electrolytic separation with a mercury cathode or the ether extraction technique is used for the removal of interfering ions and for the concentration of rare-earth metals (*e.g.*, La, Ce, Pr and Nd) before the spectrographic procedure, Th being added as the internal standard. The concentrated sample is dissolved in a small amount of HCl (1:1). An aliquot (0·05 ml) is transferred to the end of the carbon electrode and dried at 250°. An a.c. arc (6 amp.; exposure 1 min.) is used to excite the spectra. The method permits the determination of as little as 50 μg of total rare-earth metals in a 1-g sample of steel with a max. error of $\pm$ 10%.   S. H. YUEN

4413. Quick determination of the phosphorus content in steel during manufacture, with the use of the isotope dilution method. J. Fodor (Radio-isotope Lab., Csepel Iron and Metal Factory, Budapest). *Acta Chim. Acad. Sci. Hung.*, 1959, **19** (1), 13–21 (in English).—The changes in phosphorus content of steel produced by the Siemens-Martin

process are followed by introducing a drilled steel block containing a quantity of ^{32}P (0·1 mC per ton) into the molten metal; the isotope is evenly distributed within 6 min. A sample is cooled to give a casting 9 mm thick and its β-activity is measured; the test takes 5 min. and compares favourably with chemical analysis for phosphorus contents of < 0·005%. By employing standard conditions, errors due to self absorption, etc. are kept constant; an initial absolute value can be obtained by chemical means.   P. D. PARR-RICHARD

4414. Rapid determination of niobium in stainless steel. R. St. J. Emery. *Metallurgia, Manchr*, 1959, **59**, 101–103.—The spectrophotometric thiocyanate method for determination of Nb has been adapted to stainless steels. The separation and removal of interfering elements is based on the phase separation that occurs when the acid concn. of the extractant exceeds 1·4 moles per litre with acetone as the organic medium. A 20% soln. of NH_4SCN, a 10% soln. of $SnCl_2$ and a dil. soln. of H_2SO_4 (1:1) are used and the extinction is read at 383 mμ. A determination can be made within 90 min. with satisfactory reproducibility.

J. W. O. PYEMONT

4415. Rapid method for the determination of cobalt in reactor steel by activation analysis. T. Westermark and I. Fineman (Royal Inst. of Tech., Stockholm). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/140, 12 pp.—The method is based on the use of the metastable isomer ^{60m}Co which precedes the long-lived ^{60}Co after neutron capture. The ^{60m}Co emits 59-keV γ-radiation and has only 10·8 min. half-life. This enables a very short activation time to be used ($\simeq$ 10 min. in the Stockholm reactor R1 at 5×10^{11} n per sq. cm per sec.). The method has been applied to various Swedish steels. The presence of Mn is the most disturbing factor and has so far prevented the use of the direct spectrometric analytical technique (thick NaI crystal scintillation detectors and a single-channel pulse-height analyser). A rapid procedure has been used to avoid this difficulty. It involves the rapid dissolution of steel turnings in HCl, extraction of Fe into diethyl ether, and selective pptn. (after addition of carrier) of Co with nitrosonaphthol. The procedure also makes self-absorption of the soft γ-radiation negligible. A small activity of long-lived ^{60}Co is added to the dissolving acid. This is chosen so as not to disturb the spectrometry but to permit corrections for losses of Co during the procedure. The standard consists of a small filter-paper on which a small volume of cobalt soln. is evaporated. The whole procedure after activation occupies 30 to 40 min. and a sensitivity limit of 1 to 2 μg is achieved at the neutron flux used. The estimated max. error is 5 to 10% in the region 50 to 150 p.p.m. on a 1-g sample with the flux stated.   NUCL. SCI. ABSTR.

4416. Solvent extraction method for bivalent cobalt. S. Ionescu and C. Grigorescu-Sabău (Inst. de Phys. Atómica, Bucharest). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/-P/1280, 8 pp.—A comparative investigation of the extraction of Co^{2+} and Co^{3+} in the presence of each other in neutral soln. is reported. A more efficient separation method for these ions is proposed, namely the extraction of Co^{2+} as $(Co^{2+}Py_4)(SCN)_2$

with CHCl₃. The method can also be used with tracer amounts. The formation of the complex was investigated by this solvent extraction method varying each of the components in quantity, the other being in excess. In this way it was observed that the radiometric titration with NH_4SCN can be applied successfully to the quant. determination of Co^{3+}. The equilibrium shift obtained during the titration with pyridine allowed the calculation of the chemical potential for the combination of Co with pyridine to be made. NUCL. SCI. ABSTR.

4417. Separation of cobalt from nickel by means of anion exchange and the photometric determination of cobalt as the cyanate complex. M. Ziegler and W. Rittner (Anorg.-chem. Inst., Univ., Göttingen, Germany). *Z. anal. Chem.*, 1959, **165** (3), 197–200. —A column (10 ml × 1 ml) of Dowex 1-X8 (50 to 100 mesh) retains 30 mg of Co as the cyanate complex at pH 6·5 to 8, while Ni passes through. *Procedure*—The sample containing ≯ 30 mg of Co and ≯ 300 mg of Ni is neutralised with NaOH, and 40 ml of KOCN soln. (20%) and 15 ml of ammonium acetate soln. (15%) are added. The soln. (pH 6·5 to 8) is then poured through the column of Dowex 1-X8, and followed by 50 ml of H_2O. The resin is removed from the column and the Co eluted with 10 ml of HCl (20%). After neutralisation with Na_2CO_3 soln. (20%), the Co soln. is evaporated to 30 ml and transferred to a 100-ml flask; 10 ml of ammonium acetate and 40 ml of KOCN soln. are added, and the soln. is made up to vol. The extinction is measured at 620 mμ. B. B. BAUMINGER

4418. Determination of small amounts of cobalt in titanium, zirconium and their alloys. D. E. Wood and R. T. Clark (Res. Dept., I.C.I. Ltd., Metals Div., Kynoch Works, Birmingham, England). *Talanta*, 1959, **2** (1), 1–11.—Cobalt (2 to 50 p.p.m.) in titanium, zirconium and their alloys is determined absorptiometrically with nitroso-R salt at pH 6 in the presence of NH_4F. *Procedure*—Dissolve the sample (0·25 g) in H_2SO_4 (2% v/v) (10 ml) and HBF_4 soln. (1 ml). Warm to 70° to assist solution and then add several drops of conc. HNO_3, and set aside for 5 min. Add NH_4F soln. (10%) (10 ml), heat to boiling and add nitroso-R salt soln. (0·2%) (0·5 ml) and ammonium acetate buffer soln. (50%) (7·5 ml). Set aside for 5 min., add conc. HNO_3 (6 ml) and after 5 min. satd. bromine water (0·5 ml). After a further 5 min. boil for 5 min., filter into a 50-ml flask, dilute to volume and measure the extinction at 420 mμ in 4-cm cells. The method is applicable to titanium containing up to 20% of Mn, 10% of Al and 5% of Fe, and zirconium containing up to 5% of Pb, Al, Mn, Zn, Mg or W. By simple modifications samples containing 20% of Sn or Mo, 5% of Cu, Cr or V, or 2·5% of Ni can also be analysed. The standard deviation at 20 p.p.m. is $\simeq \pm 0·3$ p.p.m. W. T. CARTER

4419. Chelometric determination of cobalt and iron using a fluorescent end-point. D. H. Wilkins (Res. Lab., General Electric Co., Schenectady, N.Y., U.S.A.). *Talanta*, 1959, **2** (1), 12–15.—In EDTA titrations of Fe and Co with visual indicators the sample weight is limited to $\simeq 10$ mg because of the intense colours of the complexes of Fe and Co with EDTA. This difficulty can be avoided by using a fluorescent indicator. *Procedure*—To the slightly acid sample soln. containing up to 80 mg of Fe or Co add an excess of 0·03 M EDTA and adjust

to pH 4·8 with Na acetate - acetic acid buffer soln. Dilute to 100 ml with water, add 1 drop of calcein soln. (0·1% in 0·001 N NaOH) and back-titrate with standard Cu soln. (0·03 M) under u.v. illumination. The end-point is detected by the quenching of the green fluorescence. W. T. CARTER

4420. Determination of nickel, cobalt, iron and zinc in ferrites. D. H. Wilkins (Gen. Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (3), 271–273.—The four elements are separated by utilising the differences in adsorption of their chloride complexes on a strongly basic anion-exchange resin. *Procedure*—Dissolve the sample (1 g) in 9 N HCl (20 ml) and H_2O_2 (30%) (0·5 ml); transfer the soln. to the ion-exchange column (50 cm × 1 cm), and then elute the Ni with 9 N HCl (80 ml), the Co with 4 N HCl (75 ml), the Fe with 0·5 N HCl (100 ml), and finally the Zn with 3 N HNO_3 (100 ml). Evaporate each eluate to dryness and then determine each element by back-titration, at pH $\simeq 4·8$, of an excess (5 to 10 ml) of EDTA with 0·03 M $CuSO_4$, with 1-(2-pyridylazo)-2-naphthol as indicator. Results for Co and Fe are satisfactory, but those for Ni and Zn tend to be high. W. J. BAKER

4421. Separation of nickel and cobalt by extraction with tributyl phosphate. A. Musil and G. Weidmann (Inst. f. anorg. u. anal. Chem., Univ., Graz, Austria). *Mikrochim. Acta*, 1959, (3), 476–480.— Cobalt may be extracted from aq. soln. by means of tributyl phosphate (**I**). It is shown that even a threefold excess of Ni has little effect on the partition of Co between 8·3 N HCl and **I** - toluene (2 : 1). A method for the determination of Co in the presence of Ni is based on this finding. D. F. PHILLIPS

4422. Gravimetric determination of nickel with dimethylglyoxime in the presence of copper. A. Claassen and L. Bastings (Philips Res. Lab., Eindhoven, Netherlands). *Z. anal. Chem.*, 1959, **165** (5), 354–360 (in English).—The interference of Cu is eliminated by pptn. of Ni with dimethyl-glyoxime in a soln. containing tartrate and $Na_2S_2O_3$ at pH 5·5 to 6·5. The amount of $Na_2S_2O_3$ added (minimum 3 g) is ≮ 15 times the weight of Cu plus Fe. Brass, bronze and steel are dissolved in HCl with the addition of HNO_3. With W-containing steel the ppt. of WO_3 dissolves when the soln. is made alkaline after the addition of tartaric acid. *Procedure*—To the sample is added 5 to 10 ml of 20% aq. tartaric acid soln., the mixture is made faintly ammoniacal with aq. NH_3, filtered if cloudy, and adjusted to pH 3 to 5 with dil. HCl. After dilution to about 200 ml the soln. is heated to ≯ 45°, then 15 ml of 20% aq. $Na_2S_2O_3$ soln., and, after a few minutes, the necessary amount of 1% ethanolic dimethylglyoxime soln. are added, followed by 25 ml of 2% aq. ammonium acetate soln. (pH 6·5 to 7·0). The mixture is stirred and cooled to room temp. for ≮ 30 min., and the ppt. is collected in a sintered glass crucible, washed with cold water and dried at 150°. Results for standard samples and synthetic mixtures are tabulated. B. B. BAUMINGER

4423. Photometric determination of nickel in copper - nickel alloys. M. C. Steele and L. J. England (Metal Manufactures Ltd., Port Kembla, Australia). *Anal. Chim. Acta*, 1959, **20** (6), 555–558. —A rapid method is described for the determination

of from 1 to 32% of Ni. *Procedure*—Dissolve 1 g of the sample in 10 ml of conc. HNO_3 and boil off the nitrous fumes. Allow to cool to 80°, add 10 ml of H_3PO_4, cool to room temp. and dilute to 25 ml. Filter if necessary and measure the transmittancy at 390 mμ in a Beckman model B spectrophotometer with 2-cm cells, against a reference soln. containing approx. 1% less than the expected content of Ni. The calibration graph is prepared with soln. in which the total of Cu plus Ni is 1 g, and determinations and calibration must be conducted at the same temp. ($\pm 1°$). None of the elements likely to be present interferes, but the addition of Cl^- must be avoided.   H. N. S.

4424. Critical review of the volumetric methods for the platinum metals. F. E. Beamish (Univ. of Toronto, Ontario, Canada). *Anal. Chim. Acta*, 1959, **20** (2), 101–112.—The review covers methods for Pd, Pt, Rh, Ir, Ru and Os published up to Jan., 1958. Attention is drawn to the lack of methods generally and directly applicable to the analysis of ores, concentrates and alloys. (61 references.)   H. N. S.

4425. Quinolinic acid as a reagent for the gravimetric and volumetric estimation of palladium. A. K. Majumdar and S. P. Bag (Jadavpur Univ., Calcutta, India). *Z. anal. Chem.*, 1959, **165** (4), 247–250 (in English).—Quinolinic acid forms a complex with Pd of composition $Pd(C_7H_4O_4N)_2$, which is pptd. at an acidity of $0.25 N$ with respect to HCl or HNO_3, up to a max. pH of 2·1. Most common ions and the other platinum metals remain in soln. The only interfering ion, Cu, is eliminated by complexing with EDTA. The Pd complex is either determined gravimetrically or dissolved in standard KCN soln., which is back-titrated with $AgNO_3$ soln. Recoveries are >99% by both procedures.   G. P. COOK

4426. Separations involving palladium. Separation of lead, bismuth, cadmium, thallium, copper, cobalt and nickel from palladium. G. B. S. Salaria (Gov. Coll., Rohtak, Punjab, India). *Anal. Chim. Acta*, 1959, **20** (2), 122–123.—A soln. of $PdCl_2$ (45 to 58 mg of Pd) and Pb acetate (49 to 62 mg of Pb) in $2 N$ to $3 N$ HCl is treated with 20 ml of a 1% alcoholic soln. of dimethylglyoxime (**I**) and is set aside for 1 hr. with occasional shaking. The Pd complex is filtered off in a sintered glass crucible (porosity 4), washed with hot water acidified with HCl, then with alcohol, dried at 110° and weighed. The same procedure serves for the separation of Pd from Bi, Cd, Tl, Cu, Co and Ni. In the filtrates, Pb, Bi and Cd are determined as their sulphides, Tl as Tl_2CrO_4, Cu by thiosulphate titration, Co as the pyridine complex, and Ni with **I**.   H. N. S.

4427. Thermogravimetry of analytical precipitates. LXV. Determination of iridium. C. Duval, P. Champ and P. Fauconnier (École Nat. Supérieure de Chim., Paris, France). *Anal. Chim. Acta*, 1959, **20** (2), 152–153 (in French).—Iridium, pptd. as the metal with formic acid, yields a horizontal thermogravimetric graph up to 879°, showing that heating in hydrogen is unnecessary. The ppt. obtained with 2-mercaptobenzothiazole shows an inflection in the curve at 135° to 250°, and a horizontal portion from 520° to 980° indicates conversion into the metallic state. The ppt. obtained with Na_2S gives a constant wt. only after the free metal is formed at $\simeq 800°$.   H. N. S.

4428. New and improved methods of analysis of some nuclear raw materials. V. T. Athavale, S. Banerjee, G. K. Belekar, N. Mahadevan, L. M. Mahajan, M. N. Nadkarni, Das M. Sankar, H. D. Sharma, A. K. Sundaram, M. Sundaresan, N. R. Thakoor, M. M. Tillu, M. S. Varde and C. Venkateswarlu (Atomic Energy Estab., Trombay, India). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/1671, 15 pp.—A brief review is presented of the new and improved methods developed in the Trombay laboratory during the past few years for the analysis of minerals and ores for U, Th, Be, Nb and Ta present in macro and micro amounts. Uranium and Th determinations were also required in uranium and thorium crudes, intermediates, and pure thorium nitrate samples.
NUCL. SCI. ABSTR.

4429. Testing of nuclear fuels by the danger coefficient method. M. E. Remley and B. A. Engholm (Atomics International Div., N. American Aviation, Inc., Canoga Park, Calif.). Conf.: "Modern Approaches to the Isotopic Analysis of Uranium." Chicago, Feb. 5–7, 1957. Rep. TID-7531(Pt.2)(Del.), 53–69.—Reactors operating at essentially zero power can be used as sensitive non-destructive test-instruments for quality control and isotopic assay determinations of nuclear fuels. The use of a zero-power water boiler for this type of testing has been investigated in a series of experiments performed with the Water Boiler Neutron Source at Atomics International. Uranium cylinders, 3·875 in. in length by 0·500, 0·600 and 0·750 in. in diam., with enrichments in ^{235}U of 0·491, 0·711, 0·902, 1·399 and 2·778% by weight, have been compared by the danger coeff. method. This method with the water boiler will detect ^{235}U enrichment differences of 9×10^{-4} % by weight for samples enriched to 1% in ^{235}U and differences of 2.8×10^{-3} % by weight in samples of 3% enrichment. A suggested procedure for the application of the method to the routine testing of fuel materials is outlined.   NUCL. SCI. ABSTR.

4430. Analysis of Italian uraniferous minerals. I. Leaching with dilute sulphuric acid and concentration on exchange resins. M. L. Borlera (Politec., Turin, Italy). *Ric. Sci.*, 1958, **28** (2), 331–340.—The minerals, an Italian autunite and an Italian pitchblende, are leached with boiling N H_2SO_4. The combined extracts are adjusted to pH 1·5 to 2·1 and passed through a strong anion-exchange resin (Amberlite IRA-410), $UO_2(SO_4)_2^{2-}$ being retained and then eluted with 0·25 to 0·5 N acid ($HClO_4$, HNO_3 or HCl). Nitric acid is preferable when phosphate is to be separated from the eluate. Recovery of U of 98 to 99% from the leaching soln. is obtained. A 5-fold concn. of U in the eluate relative to that of the soln. entering the resin is obtained. Most of the phosphate accompanies the U. The Fe^{3+} are reduced to Fe^{2+} with SO_2 to avoid exchange of ferric sulphate anions. Permanganate cannot be eluted and thus may diminish the capacity of the resin. Chloride and nitrate decrease the exchangeability of the uranyl disulphate.   CHEM. ABSTR.

4431. Identification of minerals associated with asbestos by X-ray diffraction patterns. M. S. Badollet and J. P. McGourty (Johns-Manville Res. Center, Manville, N.J.). *Canad. Min. Metall. Bull.*, **51**, 335–340; *Trans. Canad. Inst. Min. Metall.*, 1958, **61**, 169–174.—Serpentine, chrysotile, antigorite, brucite, iron oxide, grammatite, epidote

and quartz were photographed by a Norelco X-ray diffraction unit with a Debye - Scherrer camera for a 4-hr. exposure by copper radiation with a nickel filter. This investigation indicates that for the complete identification of all the minerals present in samples obtained in prospecting or in drill-cores of asbestos bodies, not only chemical analyses but also the results of X-ray diffraction, spectrographic, and petrographic studies are necessary.

CHEM. ABSTR.

See also Abstracts—**4239**, Use of Zn toluene-3:4-dithiol. **4240**, Dithio-oxamide in detection of metals. **4241**, Use of sulphathiazole in inorganic analysis. **4242**, Gallein as reagent for Pb. **4246**, Separation of bivalent from tervalent ions in the presence of PO_4^{3-}. **4252**, Photometric determination of end-points in complexometric titrations. **4256**, Extraction in inorganic analysis. **4260**, Recovery of trace elements from organic materials. **4488**, Determination of Hg in paper, **4507**, Strontium in bone by X-ray fluorescence. **4605**, Determination of U in water. **4607**, Determination of Ra-C and Th-C in springs. **4608**, Determination of Ra-B and Th-B in springs. **4628**, Isotopic analysis by interferential spectrometry. **4647**, Determination of Cu and Ti. **4649**, Determination of Co.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives.

4432. The bromimetric determination of organic compounds. A. Berka and J. Zýka (Dept. Anal. Chem., Charles' Univ., Prague). *Českosl. Farm.,* 1959, **8** (1), 17–18.—It has been shown that the iodimetric titration of the excess of reagent in indirect bromimetric determinations (*e.g.*, of Na salicylate and resorcinol) can be replaced by a titration with hydrazine sulphate. *Procedure*—Dissolve the sample (0·2 to 0·5 g) in H_2O (100 ml). To 20 ml of this soln. add 0·1 N $KBrO_3$ (25·0 ml), KBr (1 g) and dil. HCl (5 ml). After 10 min. titrate potentiometrically with 0·05 M hydrazine sulphate (**I**), or add an excess of **I** and methyl red (2 to 3 drops) as indicator and back-titrate with 0·1 N $KBrO_3$ to a colourless end-point. The results were in good agreement with the iodimetric back-titration of the excess of $KBrO_3$ according to Cz.P.2.

J. ZÝKA

4433. Catalytic hydrogenation of organic compounds on paper for paper-chromatographic analysis. H. P. Kaufmann and Dipti Kalyan Chowdhury (Dtsch. Inst. Fettforschung, Munster, Germany). *Chem. Ber.,* 1958, **91**, 2117–2121.—The appropriate metallic hydrogenation catalyst, such as Pd, is produced in finely dispersed form on paper, the compound to be analysed (*e.g.*, unsaturated fatty acids, nitro compounds, nitriles, dyes) is applied to the metal spot, reduced in an atmosphere of hydrogen and chromatographed in the usual way. A 5% $PdCl_2$ soln. in 20% HCl is applied once or several times in amounts of 15 to 20 μg of Pd to both sides of a chromatographic paper at the starting line,

and dried at room temp. The paper is treated at the same places on both sides with small drops of a mixture of 80 ml of 20% aq. KOH soln. and 20 ml of 40% aq. formaldehyde soln. in such a manner that the resulting black spots due to Pd do not become larger than about 1 cm, and is then immersed for 10 min. in 5% aq. acetic acid, washed 5 or 6 times with water, pressed between filter-papers and dried at 90°. This gives the palladium paper (*A*). *A* is impregnated with undecane (previously saturated with acetic acid) and dried for 10 min. in air. A mixture of oleic (**I**), linoleic (**II**) and linolenic (**III**) acids in toluene is applied to the middle of the palladium spot and also at some distance on the base line. The paper, after being placed in a vacuum desiccator, kept for 5 min. under hydrogen, and developed with 95% acetic acid, gave 1 spot for stearic acid from the sample applied to the palladium spot and 3 spots for **I**, **II** and **III** from the palladium-free spot. The method has been applied to linseed oil. Hydrogenation reduces the spot due to oleic plus palmitic acids to one due to palmitic acid alone. The palmitic acid can thus be determined. The method has also been applied to a fish oil, sorbic acid, maleic acid, nitrobenzene, *m*-dinitrobenzene, phenyl cyanide, indigo carmine and KIO_3.

CHEM. ABSTR.

4434. Combustion of organic compounds in an oxygen atmosphere. J. Horáček (Chem. Inst., Acad. Sci., Prague). *Chem. Listy,* 1959, **53** (1), 6–9.—A survey is given of the history and extension of the Schöniger method (*Mikrochim. Acta,* 1955, 123; 1956, 869) for the determination of S in organic compounds after the combustion of the sample in an atmosphere of O. The method is considered to be reliable, simple and precise, and suitable for micro-determinations. This method can be applied to the determination of other elements (*e.g.*, F, Br, Cl, P, Hg and ^{14}C).

J. ZÝKA

4435. Determination of active hydrogen in organic compounds by exchange with tritiated isopropyl alcohol. J. F. Eastham and V. F. Raaen (Univ. Tennessee, Knoxville, U.S.A.). *Anal. Chem.,* 1959, **31** (4, Part I), 555–558.—The active hydrogen in a variety of organic compounds is exchanged for tritium from an excess of tritiated *iso*propyl alcohol by dissolving each compound in the alcohol and then evaporating the solvent. The measured activity acquired by most compounds agrees well with that expected from the number of active hydrogen atoms in the compounds, and the known radioactivity of the solvent. Data for 33 compounds are listed.

G. P. COOK

4436. Determination of carbon dioxide in the wet combustion of organic substances by the equilibration of pressures method. V. A. Semin'ko. *Trudý Khar'kovsk. Farmatsevt. Inst.,* 1957, (1), 158–159; *Ref. Zhur., Khim.,* 1959, (2), Abstr. No. 4376.—A method based on the equilibration of pressures is described for the determination of the CO_2 liberated in the oxidation of organic substances in a closed flask. A volumetric manometer to correct automatically for changes in temperature and atmospheric pressure is illustrated, and comprises a manometer with an equalising bulb and a compensating chamber. The flask with the sample and the oxidising mixture is placed near the volumetric manometer and the pressure in the compensating chamber is adjusted to atmospheric. After the combustion, the flask is connected with the manometer (the vol. of gas in the flask being increased by

the CO_2 evolved), and after equalising the pressures the amount of CO_2 is calculated by the formulae given. The error of the determination is $\pm 1\%$.

C. D. KOPKIN

4437. Organic micro-analysis. XX. Modified Dumas nitrogen determination: the correct temperature for the reduced copper. Keiichiro Hozuma and Sachiko Amako (Pharm. Inst., Med. Fac., Univ. of Kyoto, Japan). *Mikrochim. Acta*, 1959, (2), 230–242 (in English).—Apparatus and procedure are described in detail. Experiments show that the temp. of the reduced copper in the combustion tube should be maintained at 550° to 600°, in which range complete reduction of nitric oxide is attained. Above 650°, large errors due to formation of CO were observed, and, below 500°, the reduction of nitrogen oxides is incomplete.

B. B. BAUMINGER

4438. Detection and identification of halides in organic compounds. An improved micro qualitative procedure using zinc - lithium carbonate as fusion mixture. E. E. Gansel (Anal. Sect., Res. Dept., Ansco, Div. of GAF, Binghampton, N.Y., U.S.A.). *Microchem. J.*, 1959, **3** (1), 91–95.—The sample (3 to 5 mg) is intimately mixed with 25 mg of the fusion mixture (a 1:1 mixture of zinc dust and Li_2CO_3) in a heavy-walled Pyrex-glass fusion tube (75 mm × 13 mm) and a further 50 mg is placed on top. A glass-wool plug is tamped down on to the mixture, and 0·5 ml of diethyl ether added to expel air. The tube is heated to a white heat in an oxy-gas flame, commencing at the top and taking care to avoid puncture of the tube by the fused mass. The tube is then dropped into a lipped Pyrex-glass test-tube (115 mm × 26 mm) which contains 5 ml of ice-cold water and a short length of Pyrex-glass tube (17 mm × 10 mm) to break the fall and keep the hot fusion-tube from the walls of the test-tube, a cover being placed over the tube to avoid spattering. The digestion tube is swirled for 1 to 2 min., the contents are boiled and filtered, and the residue is extracted with a further 2 ml of water. The combined filtrates are then tested for halogens in the usual way. The advantages claimed are lower melting-point of the fusion mixture and low solubility of Li_2CO_3 in water. R. E. ESSERY

4439. Rapid micro-determination of fluorine in organic compounds. R. N. Rogers and S. K. Yasuda (Univ. Calif., Los Alamos, U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 616–617.—The sample is decomposed by combustion in a flask filled with oxygen at atm. pressure and the fluorine determined by an improved ferric salicylate colorimetric method. The results are generally within 3% of those expected from theory and the analysis time is 10 to 20 min. for samples of from 0·4 to 20 mg.

G. P. COOK

4440. Reduction of organic fluoro compounds with lithium and *n*-propylamine in the micro-determination of fluorine. R. D. Strahm (Redstone Arsenal Res. Div., Rohm & Haas Co., Huntsville, Ala., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 615–616.—Organic fluoro compounds are decomposed with Li and *n*-propylamine. The fluoride is separated from the residue by steam-distillation with $HClO_4$ and is determined by back-titration with $Th(NO_3)_4$ in Nessler tubes. Results are within 2% of the theoretical. G. P. COOK

4441. Semi-micro determination of fluorine and chlorine in organic compounds. III. The decomposition of fluoro and chlorofluoro compounds by the diphenyl - sodium - dimethoxyethane complex. P. Johncock, W. K. R. Musgrave and A. Wiper (Dept. of Chem., Univ., South Road, Durham, England). *Analyst*, 1959, **84**, 245–247.—The organic compound ($\equiv \simeq 8$ mg of total halogen) is dissolved in 20 ml of di*iso*propyl ether, 10 ml of a 1 to 1·5 *M* soln. of the diphenyl - sodium - dimethoxyethane complex (Liggett, *Anal. Chem.*, 1954, **26**, 269) is added and the mixture is set aside for 10 min., with occasional swirling. The liquid is extracted with water (3 × 20 ml), the combined aq. extracts are adjusted to 100 ml and a 25-ml aliquot is placed on a column of Amberlite IR-120(H). The column is eluted with 70 ml of boiled water, the eluate is heated to boiling, cooled immediately and titrated with 0·02 *N* NaOH, with screened methyl red as indicator. When more than one halogen is present the procedure of Banks *et al.* (*Anal. Abstr.*, 1956, **3**,1390) is followed. A. O. JONES

4442. New and rapid micro-analytical determination of chlorine, bromine and fluorine in organic compounds. F. Ehrenberger (Anal. Lab., Farbwerke Hoechst, A.-G., Frankfurt, Germany). *Mikrochim. Acta*, 1959, (2), 192–201 (in German).—The organic compound is vaporised in a stream of H and burnt in an oxy-hydrogen flame. The quartz combustion tube and absorber are illustrated. Chlorine and Br are determined potentiometrically with 0·02 *N* $AgNO_3$ and details of the titration of fluorine with 0·01 *N* $Th(NO_3)_4$ are given. Alkali and alkaline-earth metals interfere in the determination of halogens, and phosphate must be removed with $ZnCO_3$ before titrating with $Th(NO_3)_4$ soln. B. B. BAUMINGER

4443. Analysis for industry. A. M. G. Macdonald. *Ind. Chem.*, 1959, **35**, 33–35, 37.—A review is presented of work on the combustion of organic samples by the closed-flask technique, and applications to the determination of Hg, S, P, ^{14}C, Zn, Ca, Cd and B are described. (26 references.)

S.C.I. ABSTR.

4444. Micro-determination of the carbonyl group by oxime formation. V. A. Klimova and K. S. Zabrodina (Inst. Org. Chem., Acad. Sci., SSSR). *Izv. Akad. Nauk SSSR*, 1959, (1), 175–176.—*Procedure*—Dissolve hydroxyammonium chloride (0·7 g) in H_2O, add triethanolamine (0·5 g) and make up to 100 ml with 96% ethanol. Shake the test substance (5 to 10 mg) with this soln. (5 ml) until it dissolves and then set aside for 30 min. at room temp. Add satd. NaCl soln. (2 ml) and bromophenol blue (3 drops) to the control and titrate it with 0·02 *N* HCl. Titrate the test soln. in the same way and to the same visual end-point. The results for 12 analyses of aldehydes and ketones are tabulated. Ketones that possess methylene groups with free hydrogen atoms adjacent to the carbonyl group can be analysed by this method. K. R. C.

4445. Application of diphenylacraldehyde to functional analysis. M. Pesez and J. Bartos (Services Scientifiques Roussel-Uclaf, Paris, France). *Anal. Chim. Acta*, 1959, **20** (2), 187–189 (in French).—When 2 ml of a 1% methanolic soln. of 3:3-diphenylacraldehyde (**I**) and 1 ml of conc. HCl are added to 2 ml of a methanolic soln. of a *m*-dihydric phenol a red colour is produced. The reaction is sensitive to 1 μg of the phenol and the colour intensity follows Beer's law for 2 to 10-μg amounts. Under the same conditions **I** condenses with cyclic ketones giving yellow to yellow - green or red colours. The products of condensation with *cyclo*hexanone and barbituric acid have been

isolated, and structures have been attributed to them. Schiff's bases are formed when **I** reacts with primary aromatic amines, and the orange - yellow colours comply with Beer's law for quantities of amine up to 20 μg.   H. N. S.

4446. New method for the determination of acetyl groups. L. Mázor and T. Meisel (Tech. Univ., Budapest, Hungary). *Anal. Chim. Acta,* 1959, **20** (2), 130–133 (in German).—A rapid method is described for the determination of acetyl groups in O-acetyl compounds. The sample (45 to 300 mg) is dissolved or suspended in methanol and is saponified with 10 ml of 0·1 *N* K methoxide. The following reactions take place—

(i) $>$CH·O·CO·CH$_3$ + CH$_3$OK →
    $>$CH·O·C(CH$_3$)(OCH$_3$)(OK)

(ii) $>$CH·O·C(CH$_3$)(OCH$_3$)(OK) + CH$_3$OH →
     $>$CH·OH + CH$_3$·CO·OCH$_3$ + CH$_3$OK.
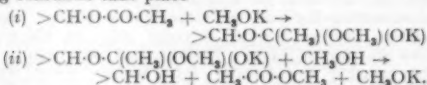
Water is then added to hydrolyse the K methoxide. The KOH so formed hydrolyses the methyl acetate and the excess of KOH is titrated with 0·1 *N* HCl, with phenolphthalein as indicator. If the reaction mixture is coloured, a fluorescent indicator is used, or the methyl acetate is distilled after the completion of reactions (i) and (ii) and the ester is hydrolysed in the distillate with an excess of 0·1 *N* NaOH. The method is applied to the acetates of several sugars, to hydroxypregnenone acetate, 3α-acetoxy-5β-ergost-22-ene, cellulose triacetate, diacetylmorphine, 2-naphthyl acetate and poly(vinyl acetate).
                                          H. N. S.

4447. Partial automation of acetyl determination: automatic control of the acetic acid distillation. G. Kainz (II Chem. Inst., Univ. Wien, Austria). *Z. anal. Chem.,* 1959, **166** (1), 32–36.—The most tedious stage in the determination of acetyl groups is the quant. distillation of acetic acid from aq. soln. containing H$_2$SO$_4$ which involves the repeated (50 to 80) additions of small quantities of H$_2$O. A device for making these additions automatically comprises a pump controlled by a relay, actuated through electrodes which operate when the liquid in the distillation flask falls below a given level. The electrodes are set to maintain a vol. of about 8 ml in the distillation flask. The distillation should take 20 to 30 min. and yield 50 to 60 ml of distillate. A modified Kjeldahl apparatus for the complete determination is described.
                                          G. BURGER

4448. Ultra-violet absorption in solvent analysis. W. Lamprecht (Inst. für Lackforsch., Giessen). *Fette, Seif., Anstrichmitt.,* 1959, **61** (2), 96–99.— The application of u.v. absorption measurements to the analysis of solvents is considered. Absorption curves for compounds typical of various solvent types (*e.g.,* aromatics, chlorinated hydrocarbons, esters, ketones and alcohols), and certain of their binary mixtures, are shown and discussed. It is concluded that u.v. spectral analysis can be a useful additional tool in the analysis of solvents, particularly when the complete separation of components is not possible by other methods. Quantitative analysis may also be possible by using the dependence of extinction on concn.
                                          S. M. MARSH

4449. Separation of C$_2$ to C$_5$ hydrocarbons by gas-liquid partition chromatography. N. M. Turkel'taub, B. I. Anvaer, A. I. Kolyubyakina and M. S. Selenkina (All-Union Sci. Res. Geological Prospecting Petroleum Inst.). *Zavod. Lab.,* 1959, **25** (2), 149–154.—Incomplete separations of C$_4$ and C$_5$ isomers,

even with optimum ratios between adsorbents and solvents. are reported. Mixed solvents, *e.g.,* dimethylformamide containing 1% of liquid paraffin on crushed brick, or dimethylformamide containing 6·5% of tri*iso*butylene on diatomite, can give complete separations of C$_4$ and C$_5$ hydrocarbons, and it is considered that conditions can be chosen for separating C$_2$ to C$_5$ hydrocarbons.
                                          G. S. SMITH

4450. Chromatographic analysis of mixtures of C$_5$ hydrocarbons. A. A. Zhukhovitskiĭ, B. A. Kazanskiĭ, O. D. Sterligov and N. M. Turkel'taub (Akad. Nauk SSSR, Moscow). *Dokl. Akad. Nauk SSSR,* 1958, **123** (6), 1037–1040.—Analytical methods for the products of the catalytic dehydrogenation of *iso*pentane into mixtures of *iso*amylenes and isoprene were investigated. The universal chromathermograph method was most convenient and the accurate calibration of chromatograms of synthetic mixtures of up to ten saturated and unsaturated C$_5$ hydrocarbons enabled this instrument to be used for the analysis of complex mixtures of C$_5$ hydrocarbons. The results were all within 3% of the correct values and the instrument was utilised for purity determinations.
                                          A. GROCHOWSKI

4451. Gas chromatography of hydrocarbons using capillary columns and ionisation detectors. A. Zlatkis and J. E. Lovelock (Dept. of Chem., Univ. of Houston, Tex., U.S.A.). *Anal. Chem.,* 1959, **31** (4, Part I), 620–621.—A 100-ft. copper capillary-column, 0·01 in. in diam., coated internally with squalane and with A as carrier gas, has been used successfully in conjunction with an ionisation detector to resolve all the C$_5$ to C$_7$ paraffins, *p*- and *m*-xylene, all the C$_1$ to C$_8$ alcohols and aq. soln. of C$_2$ to C$_5$ aldehydes. The max. load appears to be 1 μg of a mixture containing 10 components, and an efficiency of 750 theoretical plates per ft. has been reached in the separation of hydrocarbon mixtures.
                                          K. A. PROCTOR

4452. Determination of acetylene in ethylene oxide. H. L. Spell (Dow Chem. Co., Freeport, Tex.). *Anal. Chem.,* 1959, **31** (8), 1442.—Infra-red data are given.

4453. Infra-red analysis of monochloropropene mixtures. H. L. Spell (Dow Chem. Co., Freeport, Tex.). *Anal. Chem.,* 1959, **31** (8), 1442.—Infra-red data are given.

4454. Determination of ethyl bromide by means of electro-reduction. E. G. Maleeva. *Nauch. Dokl., Vÿssh. Shkol. Khim. i Khim. Tekhnol.,* 1958, (3), 505–506; *Ref. Zhur., Khim.,* 1959, (5), Abstr. No. 15,117.—A small amount of ethyl bromide (0·1 mg) is determined in a special electrolyser with platinum or nickel electrodes 4 cm apart. Reduction is carried out at 37° and with a current of 400 mA in an ethanolic medium containing 10% of alkali; the test takes 20 min. In the reaction mixture Br$^-$ are determined argentimetrically with an adsorption indicator.
                                          K. R. C.

4455. Determination of tetrabromoethane and mineral acids dissolved therein. M. Rogozinski and L. M. Shorr (Israel Mining Industries, Haifa). *Analyst,* 1959, **84**, 66–67.—The assay is based on the ease with which tetrabromoethane (**I**) is converted by alkali into CHBr:CBr$_2$ and alkali bromide. The sample ($>$150 mg of **I**) is heated to b.p. with 20 to 30 ml of methanol and titrated with 0·1 *N* NaOH to phenolphthalein indicator. When the

red colour appears, the liquid is boiled again and titration is continued until the colour is permanent after boiling for 10 sec. The determination can be checked by slight acidification of the titrated soln. with $0.1\ N$ acetic acid and titration of the alkali bromide with $0.1\ N$ $AgNO_3$, with dichlorofluorescein as indicator. The dehydrohalogenation equiv. is [wt. (g) of sample $\times$ 10,000]/vol. (ml) of $0.1\ N$ NaOH. For amounts of **I** from 2 to 150 mg, $0.01\ N$ reagents are used, the titration with alkali is taken beyond the end-point, to ensure complete dehydrohalogenation, the liquid is neutralised with $0.01\ N$ acetic acid and the alkali bromide is titrated with $0.01\ N$ $AgNO_3$. If the original sample contains HBr, excess of KIO_4 and KI are added to its soln. in methanol and the liberated iodine is titrated with $Na_2S_2O_3$ soln. A. O. JONES

4456. Detection and measurement of hydroperoxides by near infra-red spectrophotometry. R. T. Holman, C. Nickell, O. S. Privett and P. R. Edmondson (Hormel Inst., Univ. of Minnesota, Austin, U.S.A.). *J. Amer. Oil Chem. Soc.*, 1958, **35** (8), 422–425.—Hydroperoxides formed by autoxidation are characterised by absorption maxima at 1.46 and $2.07\ \mu$; the intensity of absorption is proportional to the peroxide content. The effect is not shown by dialkyl peroxides or ozonised unsaturated substances. The spectral detection of –OOH is not possible when the peroxide value is <500 milli-equiv. per kg.

P. D. PARR-RICHARD

4457. Organic chemical microscopy. IV. 3:5-Dinitrobenzoates of hydroxy compounds in qualitative organic analysis. R. E. Dunbar and F. J. Ferrin (North Dakota State Coll., Fargo, U.S.A.). *Microchem. J.*, 1959, **3** (1), 65–82.—Alcohols, glycols, phenols and related compounds are purified, and 1 ml of a liquid, or 0.5 g of a solid dissolved in diethyl ether, is treated with metallic sodium till no further reaction is observed. If the reaction mixture is solid, a little of the original liquid, or of ether, is added to give a semi-liquid mass, to which 0.15 g of 3:5-dinitrobenzoyl chloride is added, with stirring and cooling if necessary. Water (10 ml) is added and the whole allowed to crystallise. The crystals are filtered off, triturated with 10 ml of 2% aq. Na_2CO_3 soln. and re-filtered. The crystals are dissolved in acetone and allowed to crystallise after filtering. (When only oily drops are formed, the mixture is extracted with ether, the ether evaporated, and the residue crystallised from ethanol, but rapid manipulation is necessary to avoid esterification.) The derivatives are re-crystallised from acetone and examined at a magnification of $\times$ 150. Photographs are given of derivatives from 40 single compounds, 8 binary and 1 ternary mixture. The results are discussed.

R. E. ESSERY

4458. Effect of sodium borate on the optical rotation of sugars. R. C. Hughes and W. J. Whelan (Lister Inst. of Preventive Med., London). *Chem. & Ind.*, 1959, (2), 50.—The changes in optical rotation which occur in $0.6\ M$ borate buffer at pH 10 are listed for 29 mono-, di- and tri-saccharides.

K. A. PROCTOR

4459. Separation and determination of isomaltose and gentiobiose. Nobuko Seno (Zool. Lab., Fac. Sci., Ochanomizu Univ., Tokyo). *Nat. Sci. Rep., Ochanomizu Univ.*, 1958, **9** (2), 57–60.—Paper chromatography and paper electrophoresis have been used to identify isomaltose (α-1:6) and gentio-

biose (β-1:6). Electrophoresis on Whatman No. 1 paper in a borate buffer (pH 9.8) is more suitable than paper chromatography. For their quant. determination, ion-exchange chromatography is employed using the borate complexes on a strong base anion exchanger (Dowex 1). (17 references.) (From English summary.) S.C.I. ABSTR.

4460. A remark on the refractive-index increment of dextran for the molecular-weight determination by light scattering. M. Zebec, G. Deželić, J. Kratohvil and K. F. Schulz (Dept. of Phys. Biochem., "Andrija Štampar" Sch. of Public Health, Univ. of Zagreb, Yugoslavia). *Croat. Chem. Acta*, 1958, **30** (4), 251–255 (in English).—Values have been determined for the refractive-index change with concn. (dn/dc) for aq. dextran soln. at $436\ m\mu$, $546\ m\mu$ and $578\ m\mu$. The dextran was dissolved by pouring the powder into boiling water and heating for 2 hr. in a water bath at $100°$. The concn. of the soln. was found by drying an aliquot in a vacuum oven over P_2O_5 at $110°$. $\triangle n$ was measured for a series of soln. of various concn. by means of an interferometer, the wavelength being selected with a mercury vapour lamp and suitable filters. The values found for dn/dc (cu. cm per gram) were— at $436\ m\mu$, 0.1518 ± 0.0012; at $546\ m\mu$, 0.1481 ± 0.0013; at $578\ m\mu$, 0.1476 ± 0.0013. H. M.

4461. Analysis of sodium formaldehyde-bisulphite and sodium formaldehydesulphoxylate (rongalite). L. Maros (Inst. f. Anorg. u. Anal. Chem., L. Eötvös Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1959, **19** (1), 57–64 (in German).—This is a German version of the article published originally in Hungarian in *Magyar Kém. Foly.*, 1958, **64**, 41 (*cf. Anal. Abstr.*, 1958, **5**, 3779).

P. D. PARR-RICHARD

4462. Quantitative determination of trace amounts of carbonyl compounds. II. Colorimetric analysis for acetaldehyde. E. W. Malmberg, B. Weinstein, D. L. Fishel and R. A. Krause (Dept. of Chem., Ohio State Univ., Columbus, U.S.A.). *Mikrochim. Acta*, 1959, (2), 210–213 (in English).—The method is based on the addition of 2-(4-phenylazo)phenylhydrazinesulphonic acid to the strongly acid acetaldehyde soln. and extraction of the lavender-coloured product with $CHCl_3$ in the presence of ethanol. Procedures for concn. of $25\ \mu$g per ml and of 1 to $5\ \mu$g per ml of aldehyde are described. The aldehyde can be determined with an accuracy within ± 0.5 p.p.m. B. B. BAUMINGER

4463. General survey of the characterisation and determination of acids and acid anhydrides. S. Veibel (Tech. Univ., Copenhagen, Denmark). *Chim. Anal.*, 1959, **41** (1), 12–17.—A literature survey is presented, and procedures are outlined for the identification of acids by the formation of salts, esters, amides and anilides, the identification of amino acids, the use of partition chromatography, the identification of acid anhydrides, and the detection and identification of acids and alcohols combined as esters. Forty-nine references are numbered but not otherwise identified.

R. E. ESSERY

4464. Micro-titration of weak organic acids in non-aqueous solvents. R. K. Maurmeyer, M. Margosis and T. S. Ma (Dept. of Chem., Brooklyn Coll., New York City, U.S.A.). *Mikrochim. Acta*, 1959, (2), 177–191 (in English).—The titration vessel (50 ml) has five necks, one in line with the vertical axis of the flask and the other four equally

spaced and slightly oblique. The vertical neck has a glass joint for the micro-burette, and two diametrically opposed side openings are used for electrodes. A stream of N passes through the other two openings to minimise interference by CO_2. Visual titrations in dimethylformamide (I), pyridine (II), ethylenediamine and 3-methylbutan-2-one (III), with thymol blue and azo violet as indicators, are described. II is used for the titration of organic acids that are too weak to be titrated accurately in I (e.g., sulphanilamide). Visual titrations in I are employed for compounds with pK_a values of $\simeq 9$ and potentiometric titrations for those with pK_a of $\simeq 10.5$. With thymol blue as indicator, compounds with a pK_a of $\simeq 9$ can be titrated in III.
B. B. BAUMINGER

4465. **Behaviour of acidic organic compounds in non-aqueous media on ion-exchange resins.** R. N. Shelley and C. J. Umberger (Hosp. for Special Surgery, New York, U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 593–595.—Compounds of different acidity are adsorbed on strongly basic ion-exchange resins and eluted with ethanol or acidic ethanol; the individual fractions are identified by u.v. spectrophotometry. Recoveries were $> 93\%$ for the 20 compounds tested.
G. P. COOK

4466. **Titration of mixtures of amines in a non-aqueous medium.** E. A. Gribova and É. S. Levin (K. E. Voroshilov Inst. of Org. Intermediates and Dyestuffs). *Zavod. Lab.*, 1959, **25** (1), 38–41.—The potentiometric titration with $0.1\ N$ $HClO_4$ in dioxan of an acetone soln. of a mixture of *cyclo*- and di-*cyclo*-hexylamines and aniline gives two potential jumps, the first corresponding to the content of *cyclo*hexylamines and the second to that of aniline. If salicylaldehyde is first added, the single potential jump obtained corresponds to the content of di-*cyclo*hexylamine alone. Hence from the results of two titrations the amounts of all three components can be determined.
G. S. SMITH

4467. **p-Chlorobenzoyl isothiocyanate as reagent for characterisation of primary and secondary amines.** M. Tišler (Univ. of Ljubljana, Yugoslavia). *Z. anal. Chem.*, 1959, **165** (4), 272–275.—*p*-Chorobenzoyl *iso*thiocyanate reacts almost quant. with primary and secondary amines in the cold. The derivatives are re-crystallised from ethanol and are identified by their m.p. Data for $\simeq 50$ amines are listed.
G. P. COOK

4468. **Identification of secondary β-hydroxyethylamines by fluorescence, polarography, paper chromatography and thermochromy.** K.-H. König and H. Berg (Inst. f. Mikrobiol. und exper. Therapie, Jena, Germany). *Z. anal. Chem.*, 1959, **166** (2), 92–100.—Compounds of the general formula $HN(R)\cdot CH_2\cdot CH_2\cdot OH$ can be identified by reaction with excess of *p*-benzoquinone (or preferably 1:4-toluquinone) in ethanol or acetone; the products (2-substituted quinones) are formed rapidly and behave characteristically. They are separated from 2:5-di-substituted by-products by paper-disc chromatography, and give a yellow zone strongly fluorescent in u.v. light. Brief warming changes the yellow to violet (thermochromic change) and the change is reversible (but not after prolonged warming). On polarography the substances show a characteristic two-electron equilibrium doublet. In this way 10^{-5} to 10^{-6} g of hydroxy-amine can be identified. Primary 2-hydroxyethylamines give 2:5-di-substituted benzoquinones only; tertiary 2-hydroxyethylamines do not react.
J. P. STERN

4469. **Determination of small amounts of tri-isooctylamine in aqueous solution.** A. W. Ashbrook (Res. and Devel. Div., Eldorado Mining and Refining Ltd., Ottawa, Ontario, Canada). *Analyst*, 1959, **84**, 177–179.—The method was developed for the determination of tri-*iso*octylamine (I) in aq. soln. resulting from the extraction of uranium-bearing ores. To the sample soln. NaH_2PO_4 is added [to prevent formation of $Fe(SCN)_3$] and 20 ml of a soln. of $Co(NO_3)_2$ and $NaSCN$ (10 g of each in 100 ml of water) and the mixture is shaken. It is then extracted with a known vol. of CCl_4 and the extinction of the separated and filtered organic layer is measured at $620\ m\mu$ and referred to a calibration graph. The standard soln. for calibration are prepared by dissolving 0.5 g of I in 1 litre of methanol, acidifying portions of this soln. with 2.5% H_2SO_4 (10 ml), diluting to 80 ml and developing and extracting the Co complex as with the sample soln. The method is satisfactory for determining up to 5 mg of I.
A. O. JONES

4470. **Methods used in industry for the determination of the aromatic hydroxyl function.** R. Goupil and G. Mangeney. *Chim. Anal.*, 1959, **41** (1), 18–22.—In the control laboratory, three methods are used, namely (i) *acetylation*, on the macro or micro scale, which determines the hydroxyl group directly, (ii) *coupling*, which is an indirect method only, and (iii) *esterification*, which determines the hydroxyl group directly, and can to some extent distinguish between aromatic and non-aromatic hydroxyl groups. These methods are outlined, with references and notes. With respect to the analytical laboratory, it is noted that, since it usually deals only rarely with pure chemicals, it is usually necessary to isolate, and identify qualitatively, the constituents possessing aromatic hydroxyl groups, before the analysis proper. The importance of the assistance given by spectrophotometric and allied techniques and chromatographic procedures is briefly noted. (36 references.)
R. E. ESSERY

4471. **Anomalous alkoxyl values for tert.-butyl-substituted phenols.** A. D. Campbell and V. J. Chettleburgh (Microanal. Lab., Chem. Dept., Univ. of Otago, Dunedin, New Zealand). *Analyst*, 1959, **84**, 190–193.—The high values obtained when Zeisel's method as modified by Vieböck and Schwappach (*Ber.*, 1930, **63**, 2818) is used on the micro scale for the determination of alkoxyl groups in *tert.*-butyl-substituted phenols can be avoided by replacing the 25% Na acetate soln. used in the scrubber by a mixture of equal vol. of 5% soln. of $CdSO_4$ and $Na_2S_2O_3$. The apparatus is a slight modification of that of Elek (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 174). A 30-ml portion of phenol is added to the sample and then $\simeq 0.2$ ml of 30% H_3PO_2 and 1 ml of HI. The liquid is gently refluxed with CO_2 passing at $\simeq 4$ ml per min. The scrubber contains 2 ml of the $CdSO_4 - Na_2S_2O_3$ soln. and the absorber contains 5 ml of a soln. prepared by adding 10 drops of Br to glacial acetic acid containing K acetate. The contents of the absorber are added to 2 ml of 25% aq. Na acetate soln., Br is destroyed with formic acid, 50 ml of 10% H_2SO_4 is added and the liberated iodine is titrated with $0.02\ N$ $Na_2S_2O_3$.
A. O. JONES

4472. **Rapid analysis of metol and quinol.** Chien-Teh Soong. *Cinema Tech.*, 1958, (10), 25–26.—The method is based on the fact that metol is insol. in ethyl acetate. The sample containing metol and quinol is shaken with ethyl aectate, then H_2SO_4 or

HCl is added, and the various layers are separated and titrated with $Ce(SO_4)_2$ soln. The procedure is described. The end-point is sharp and the error is $<2\%$. The time required for the determination is only 10 to 11 min.　　　　SCI. ABSTR. CHINA

4473. Quantitative analysis of mono- and poly-basic carboxylic acids in potassium bromide discs by infra-red spectroscopy. D. E. Nicholson (Humble Oil and Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 519–523.—The method utilises the pressed-disc technique with careful control of mixing time, die pressure and pressing time; the critical variable is mixing time. The method was applied to 8 acids (derived from 1:2:4-trimethylbenzene and the three tetramethyl-benzenes) in admixture and gave an over-all precision of $\pm 5\%$. The accuracy was generally better than $\pm 10\%$ for normalised compounds. Wavelength data are listed and some anomalies in the spectra are discussed.　　　　G. P. COOK

4474. Determination of the nitrating agent requirements of organic compounds for analytical purposes. G. Halfter (J. R. Geigy A.-G., Grenzach/Baden, Germany). *Z. anal. Chem.*, 1959, **165** (4), 275–277.—Two methods are described. (*i*) The substance is mixed with H_2SO_4 in a nitrometer, a known excess of HNO_3 is added and the mixture is set aside to allow the nitration to take place. The excess of HNO_3 is then measured by the usual nitrometer procedure, and deducted from a blank conducted in the absence of the test substance. This procedure is applicable to easily nitrated substances. (*ii*) The nitrating acid is added from a burette to the substance in conc. H_2SO_4 maintained under suitable nitrating conditions, the potential being measured by a platinum - calomel electrode pair, and the "Colcra-Redoxomaten" (Halfter and Köhler, *Chem.-Ing.-Tech.*, 1958, **31**, 340) is introduced. This measures out the nitrating agent according to the reaction velocity, and shuts off the supply precisely at the end of the nitration. This apparatus not only enables the total requirement to be determined rapidly, but, in the case of substances which are nitrated in stages, enables the portion still unused to be rapidly and certainly determined.
　　　　G. P. COOK

4475. Quantitative determination of the three isomeric chloronitrobenzenes when present together by using infra-red absorption spectra. V. A. Pozdyshev and É. S. Levin (K. É. Voroshilov State Scientific-Res. Inst. of Organic Intermediates and Dyestuffs, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (1), 128–132.—The i.r. absorption spectra of *o*-, *m*- and *p*-chloronitrobenzene in CCl_4 differ in having peaks at the following frequencies—*o*-isomer 1053 cm^{-1}; *m*-isomer 1063, 917 and 879 cm^{-1}; *p*-isomer 533 cm^{-1}. Calibration curves are constructed for the percentage (w/v) of the *m*- and *p*-isomers *vs.* percentage transmission at 879 and 533 cm^{-1}, respectively. With a content of *m*-isomer of 0·5 to 3% the error is $\geqslant 10\%$ (relative); if the content is $>5\%$ the error is about 1%. The absorption of the *m*-isomer at 917 cm^{-1}, though weak, may be used as a qual. test.　　　　C. D. KOPKIN

4476. Spectrophotometric determination of poly-cyclic aromatic hydrocarbons. A. J. Lindsey (Sir John Cass Coll., London, England). *Anal. Chim. Acta*, 1959, **20** (2), 175–181.—Previously published methods for the chromatographic separation and

spectrophotometric determination of μg quantities of polycyclic aromatic hydrocarbons (*cf.* Commins *et al.*, *Brit. J. Cancer*, 1954, **8**, 296) are elaborated. The methods are here applied to samples of carbon black, soot, solids from air, smoke from tobacco and wood, coal tar and a wide variety of substances that have been treated or contaminated with smoke. The chromatographic elution sequence is given for 22 hydrocarbons, together with their u.v. absorption characteristics.　　　　H. N. S.

4477. Detection of anthraquinone and anthracene in spot-test analysis. F. Feigl and E. Jungries (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Microchem. J.*, 1959, **3** (2), 213–214.—*Procedure*—Mix in a micro test-tube a few micrograms of anthraquinone or a derivative with 1 drop of $5 N$ NaOH and several centigrams of $Na_2S_2O_4$, and warm over a micro flame. A more or less intense red colour appears rapidly. For anthracene, allow a drop of benzene or ether soln. containing 5 to 10 μg of the compound to evaporate to dryness. Test the residue for anthraquinone. The limits of detection are (in μg)—anthraquinone, 0·5; anthracene, 5·0; 1-aminoanthraquinone, 1·0; 2-chloro-3-methylanthraquinone, 2·0; anthra-quinone-1- and -2-sulphonic acids, 1·0; and anthra-quinone-1:5- and -2:6-disulphonic acids, 2·0.
　　　　D. F. PHILLIPS

4478. Separation and identification of carcino-genic polynuclear aromatic and related compounds by paper chromatography: 9-anthraldehyde, 1:9-benzanthrone, 3:4-benzopyrene, chrysene, 1:2-5:6-dibenzanthracene, 3-methylcholanthrene, phenan-thraquinone and pyrene. L. C. Mitchell and D. Banes (Div. Food, Food and Drug Admin., Wash-ington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1959, **42** (1), 161–168.—The compounds named may be separated on paper impregnated with dimethyl-formamide in diethyl ether, development being effected with 2:2:4-trimethylpentane. Altern-atively, but less satisfactorily, soya-bean oil in diethyl ether is used for impregnation and aq. *iso*propyl alcohol or *n*-propanol for development. The chromatograms are viewed in light of wave-length 3660 A or 2537 A. The use of a chromogenic spray of tetrachlorophthalic anhydride in acetone improves the identification.　　　　A. A. ELDRIDGE

4479. Diagnostic reactions for the pentacyclic triterpenes. M. Shamma (State Univ., University Park, Pa., U.S.A.). *Drug Standards*, 1959, **27** (2), 42–49.—The reactions of the following reagents with terpenes of the amyrane, oleanane and lupane groups are reviewed—bromine, hydrogen (catalytic hydrogenation), cold perbenzoic acid, ozone, selen-ium dioxide in acetic acid, N-bromosuccinimide and strong acids.　　　　A. R. ROGERS

4480. Detection and determination of pyridine and its derivatives. W. Nielsch (J. A. Benckiser Co., Ludwigshafen, Germany). *ChemikerZtg*, 1958, **82**, 137–138.—The method makes use of the colour change (red to violet) when pyridines are treated in a pH 5 buffer with ClCN, formed *in situ* from chloramine T and KCN. Nicotinic acid, its deriv-atives and *iso*nicotinic acid (**I**) give colours, but carbonyl derivatives of isoniazid fail to give a colour until after oxidation with Ce^{2+}. The determination of **I** in the range 0·001 to 0·005 mg is described.
　　　　CHEM. ABSTR.

4481. Titanometric determination of the N-oxide group in pyridine N-oxide and related compounds. R. T. Brooks and P. D. Sternglanz (Olin Mathieson Chem. Corp., New Haven, Conn., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 561–565.—The functional N-oxide group is quant. reduced by TiCl$_3$ with a two-electron change, and a 5-min. reaction period is adequate for most of the compounds investigated. The excess of TiCl$_3$ is determined by titration with $(NH_4)_2SO_4.Fe_2(SO_4)_3$ to an orange - red end-point, and a blank determination is run under the same conditions as for the sample. Several compounds require the presence of a complexing agent (citrate or SCN⁻) during the reduction. The precision and accuracy are within ± 1% and the results agree well with those obtained by other methods.   G. P. Cook

4482. Determination of sulphur traces in naphtha by lamp combustion and spectrophotometry. R. W. Klipp and J. E. Barney, II [Res. Dept., Standard Oil Co. (Indiana), Whiting, U.S.A.]. *Anal. Chem.*, 1959, **31** (4, Part I), 596–597.—The method described can be used to determine S in concn. from 1 to 400 p.p.m. After burning the naphtha sample in an ASTM lamp combustion apparatus, the H_2SO_4 formed is treated with Ba chloranilate to form chloranilic acid, which absorbs at 330 mμ and 530 mμ. By using a buffer (0·1 M in both acetic acid and Na acetate) the need to adjust the pH is eliminated. The method is more precise than, at least as accurate as and four times as sensitive as the widely used method of lamp combustion and turbidimetry.   K. A. Proctor

4483. Potentiometric titration of coal in a non-aqueous medium. W. J. S. Pringle (Coal Survey Lab., Nat. Coal Board, Birmingham, England). *Nature*, 1959, **183**, 815–816.—Groups containing acidic oxygen are determined in coal with *n*-butylamine as solvent and Na methoxide in benzene - methanol as titrant. The progress of the titration is followed potentiometrically. Sixteen coals of various ranks and carbon content were analysed; those of high carbon content (>90%) showed little or no differentiation and a low acidity, whilst those of low carbon content (79 to 86%) had a higher acid content; the curves, however, were difficult to interpret.   G. P. Cook

4484. Determination of iodine affinity of starch by amperometric titration. Masaharu Ito and Shigekazu Yoshida (Fac. of Agric., Univ. of Agric. and Technol., Fuchu, Tokyo). *Bull. Agric. Chem. Soc. Japan*, 1959, **23** (1), 34–39 (in English).—Starch was titrated with iodine, with a rotating platinum electrode and a S.C.E. No external e.m.f. was applied and the only instrument necessary was a sensitive galvanometer. By plotting free iodine against added iodine a sharper end-point was obtained than by the potentiometric routine of Bates *et al.* (*J. Amer. Chem. Soc.*, 1943, **65**, 143). The disadvantage of the amperometric titration was the variability of electrode sensitivity. The method was used to follow the change of iodine-binding capacity of whole and fractionated starches during β-amylolysis.   E. Dux

4485. New columnar and mixed-bed ion-exchange methods for surfactant analysis and purification. M. E. Ginn and C. L. Church (Monsanto Chem. Co., Dayton, Ohio, U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 551–555.—The analysis of mixed anionic and non-ionic detergents is based on the adsorption of the anionic material on an ion-exchange resin after removal of cations on a strongly acid resin. The non-ionic detergent remains in the percolate and is recovered. The anionic material is eluted from the column with NaOH [2% in *iso*propyl alcohol - water (1 : 1)] and is finally isolated as a sodium salt. A mixed-bed batch method is also given for the rapid purification and analysis of non-ionic surfactants. The accuracy for both methods is within ± 5%.   G. P. Cook

4486. The equivalent weights of wetting agents. G. Russell and E. Whittaker (Ramsden Lab., Ilford Ltd., Woodman Rd., Brentwood, Essex, England). *Analyst*, 1959, **84**, 253–254.—A column of Zeo-Karb 225 is converted into its H form by passing 3 N HCl through it and then washing it free from acid. The column is then warmed by passing water at 60° through it. A warm aq. soln. of 0·5 g of the wetting agent in 50 ml is applied to the column followed by warm water until 200 ml of eluate has been collected. This is titrated with 0·1 N NaOH, with methyl red as indicator. Water (50 ml) is used in place of the sample soln.to determine the blank value of the resin bed. Results with both anionic and cationic wetting agents show satisfactory agreement with those of other methods except with Teepol 530, this exception being due to the presence of potassium salts in the product.

A. O. Jones

4487. Use of phthalic anhydride for determining degree of substitution in hydroxyethylcelluloses. J. Quinchon. *Compt. Rend.*, 1959, **248** (2), 225–228. —After reaction with a fivefold excess of a 5% (w/v) soln. of phthalic anhydride in pyridine at 40° for ≃5 hr., all the substituent hydroxyl groups in a hydroxyethylcellulose are neutralised. The degree of substitution of the sample can be then determined by back-titrating the unused phthalic anhydride with 0·2 N NaOH. The substitution modulus (obtained by an alkoxyl determination) of the sample should be known. For samples having degrees of substitution of ≃0·7, the accuracy is within 6%, but falls to ±12% when the degree of substitution is only ≃0·3.   W. J. Baker

4488. Determination of microgram quantities of mercury in paper. L. G. Borchardt and B. L. Browning (Inst. Paper Chem., Appleton, Wis.). *TAPPI*, 1958, **41** (11), 669–671.—Mercury (1 to 10 p.p.m.) is determined in 1 g of paper by burning the sample in an oxygen bomb containing 15 ml of 0·1 N KMnO$_4$ and 10 ml of 10% H_2SO_4. After ignition of the paper, the bomb is shaken for 2 min., the pressure is released and the contents are transferred to a separating-funnel. Hydroxyammonium sulphate soln. (20%) (5 ml) is added, followed by 5 ml of dithizone soln. (10 p.p.m. in CHCl$_3$). The extinction of the CHCl$_3$ layer is measured against the dithizone soln. at 490 mμ.   W. Holden

4489. Methoxyl groups in wood—Revision of official standard T2m-43. *TAPPI*, 1958, **41**, 168A–170A.—The new method is adopted from ASTM D914–50 and the apparatus and reagents of T2m-43 are changed. The principle is the same as in the original Zeisel method except that the CH$_3$I is collected in an acetic acid soln. of K acetate [100 g of anhyd. K acetate in 1 litre of a soln. containing glacial acetic acid (900 ml) and acetic anhydride (100 ml)] containing bromine. The apparatus consists of a reaction flask with side-arm for the admission of CO$_2$, an air condenser with

trap, and a receiver. The trap is half filled with re phosphorus slurry (0·06 g, in 100 ml of H_2O) and 19 to 20 ml of bromine soln. (5 ml of bromine in 145 ml of K acetate soln.) is placed in the receiver. The weighed specimen, in a gelatin capsule, is heated in the reaction flask on an oil bath at 150° for 40 min. with 2 ml of phenol or, preferably, propionic anhydride, and 6 ml of HI, while CO_2 is passed through. The receiver contents are washed into 10 ml of 22% Na acetate soln., and 90% formic acid soln. is added dropwise until the colour is discharged, followed by 6 drops in excess. After 3 min., 3 g of KI and 15 ml of H_2SO_4 (1:9) are added, and the soln. is titrated in the usual manner with 0·1 N $Na_2S_2O_3$. Results from a blank carried out with a gelatin capsule and 2 ml of propionic anhydride are deducted.   R. Aicher

4490. Microscopic identification of man-made fibres from the criminalistics point of view. A. Longhetti and G. W. Roche (State Crime Lab., St. Paul, Minn.). *J. Forensic Sci.*, 1958, **3**, 303–329. —A scheme for the identification of 18 common synthetic fibres is presented. The scheme requires microscopic examination of longitudinal sections; optical properties such as sign of elongation, birefringence, refractive index; m.p. and eutectic-point with *p*-nitrophenol; solubility and density. Most common synthetics are probably identifiable by this suggested scheme. Single fibres are adequate for the analysis. Difficulties are en-countered only with some deeply dyed fibres, particularly black ones.   Chem. Abstr.

4491. Determination of low chlorine concentrations in plastics. D. M. Colman (Radiation Lab., Univ., Livermore, Calif.). *U.S. Atomic Energy Comm.*, Rep. UCRL-5346, 1958, 5 pp.—The method is based on combustion in a Parr oxygen bomb, an ion-exchange step to remove interfering cations, and a mercuric perchlorate titration, with diphenyl-carbazide as indicator. The precision is of the order of 0·005%.   Nucl. Sci. Abstr.

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method gives results agreeing with those by the method of Riess and Papayannis and has the advantage that triethanolamine is non-volatile.
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4500. Alkalimetric determination of sodium in ball propellents. G. Norwitz (Pitman-Dunn Lab., Frankford Arsenal, Philadelphia). *Anal. Chem.*, 1959, **31** (4, Part I), 574–578.—Sodium sulphate is used as a peptising agent in ball propellents. An improved method for its determination by pptn. as sodium zinc uranyl acetate (**I**) and titration with NaOH is proposed; the effects of temp. and time on the pptn. of the sodium salt, and of soln. and titration vol. on the volumetric stage are discussed. *Procedure*—Heat the sample (10 g) with HNO_3 (70 ml) for 15 min. and evaporate to incipient dryness. Add HNO_3 (30 ml) and 70% $HClO_4$ (7 ml) to the moist · residue in a covered beaker and evaporate to fumes. Remove the cover and evaporate to dryness; add H_2O (15 ml), cover and boil for 3 min. Cool and filter to remove graphite, evaporate the filtrate to 5 ml, wash down the beaker with H_2O and evaporate to 3 ml. To the warm soln. add 20 ml of zinc uranyl acetate soln. and set aside for ≮ 1 hr. Filter through a medium sintered glass crucible and wash with satd. ethanolic **I** soln. Dissolve the ppt. in H_2O (50 ml), add phenolphthalein and titrate with 0·1 N NaOH. Perform a blank determination. The standard deviation was ± 0·0024 (11 determinations) for a sample containing 0·06% of Na_2SO_4.
P. D. PARR-RICHARD

See also Abstracts—**4254**, Chronopotentiometric determination of mercaptobenzothiazole and other

oxidisable org. compounds. **4367**, Determination of S in org. compounds. **4402**, Iodide in photographic soln. **4609**, Anionic detergents in water and sewage. **4619**, Dust-free evaporation of soln. for crystallisation.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

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4502. Rapid determination of calcium in biological material. H. D. Appleton, M. West, M. Mandel and A. M. Sala (Dept. of Clin. Chem., Met. Hosp., New York, U.S.A.). *Clin. Chem.*, 1959, **5** (1), 36–44. —The serum (0·1 ml) or urine (0·5 ml) is titrated with EDTA soln., with calcein as indicator.
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4503. Automatic titration of calcium or magnesium in blood serum. H. V. Malmstadt and T. P. Hadjiioannou (Dept. of Chem., Univ. of Illinois, Urbana, U.S.A.). *Clin. Chem.*, 1959, **5** (1), 50–56.— The use of the Sargent - Malmstadt "Spectro" titrator is described. The titration of Ca is carried out at pH 13 with EDTA, with Calcon (*cf.* Hildebrand and Reilley, *Anal. Abstr.*, 1957, **4**, 2518; Lott and Cheng, *Ibid.*, 1957, **4**, 3576) as indicator; Ca and Mg are titrated together with EDTA at pH 10, with Eriochrome black T as indicator. A single determination takes about 5 min.
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trap, and a receiver. The trap is half filled with re phosphorus slurry (0.06 g, in 100 ml of H_2O) and 19 to 20 ml of bromine soln. (5 ml of bromine in 145 ml of K acetate soln.) is placed in the receiver. The weighed specimen, in a gelatin capsule, is heated in the reaction flask on an oil bath at $150°$ for 40 min. with 2 ml of phenol or, preferably, propionic anhydride, and 6 ml of HI, while CO_2 is passed through. The receiver contents are washed into 10 ml of 22% Na acetate soln., and 90% formic acid soln. is added dropwise until the colour is discharged, followed by 6 drops in excess. After 3 min., 3 g of KI and 15 ml of H_2SO_4 ($1:9$) are added, and the soln. is titrated in the usual manner with $0.1 N$ $Na_2S_2O_3$. Results from a blank carried out with a gelatin capsule and 2 ml of propionic anhydride are deducted.   R. AICHER

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Rep. A/CONF.15/P/549, 7 pp.—The advantages of the method previously described (*Anal. Abstr.*, 1958, **5**, 3184) are discussed.

4507. Estimation of strontium in animal bone using X-ray fluorescence analysis. W. M. B. Roberts (Bur. of Min. Resources, Canberra, Australia). *Nature*, 1959, **183**, 887–888.—Unlike other methods of determining Sr in biological material, this method does not require destruction of the sample. The spectra of the major constituents, Ca and P, do not interfere with the Sr K_α line used and the effect of any heavier elements can be ignored because of their low concn. No internal standard is necessary. A special method of sample preparation designed to ensure absolute reproducibility is described. K. A. PROCTOR

4508. Determination of thorium in urine. G. A. Welford, D. C. Sutton, R. S. Morse and S. Tarras (U.S. Atomic Energy Comm., N.Y.). *Amer. Ind. Hyg. Ass. Quart.*, 1958, **19**, 464–468.—Based on the biochemical similarity of Th and Pu, the indicated minimum sensitivity required to study the excretion rate and body burden of Th is $0 \cdot 2$ μg per litre of urine. Several spectrophotometric methods are capable of detecting this quantity of Th. Procedures for using these methods are detailed, and results are given from analyses in which Chrome azurol S (C.I. Mordant Blue 29), thoron and morin were used. NUCL. SCI. ABSTR.

4509. Determination of iron in horse serum. I. Ruždić and V. Gregorovič (Cent. Med. Chem. Lab., Zagreb). *Mikrochim. Acta*, 1959, (2), 294–298 (in German).—The method is based on the formation of a coloured complex with 2:2'-dipyridyl reagent (**I**) ($6 \cdot 6045$ g of Na acetate is dissolved in 9 ml of glacial acetic acid, $0 \cdot 5$ g of 2:2'-dipyridyl is added and the soln. is diluted to 100 ml). *Procedure*—Serum (2 ml) is mixed with 6 ml of H_2O and 2 ml of aq. trichloroacetic acid soln. (20%) in a test-tube and heated in a water bath at 90° to 95° for 10 min., with occasional shaking. The mixture is then cooled to room temp. and filtered. An aliquot (5 ml) of the filtrate is transferred to a test-tube and 2 ml of **I**, 2 ml of fresh aq. quinol soln. (2%) and $7 \cdot 5$ ml of H_2O are added. A blank determination is carried out at the same time. The extinction is measured at 520 mμ and the concn. of Fe determined by reference to a calibration graph. E. B. BAUMINGER

4510. Paper-chromatographic determination of mono- and oligo-saccharides in green plants and fruits. F. Scheffer, E. Welte and K. Müller (Agrik.-chem. u. Bodenkundl. Inst., Univ. Göttingen, Germany). *Z. anal. Chem.*, 1959, **165** (5), 321–337. —Of the three procedures examined, the freezing process has been found advantageous in eliminating changes in the carbohydrate content of green plants and rendering physiological processes inactive. Apparatus for extraction and elution, and paper-chromatographic separation for the qual. and quant. determination of saccharides are described in detail. The limit of error is ± 2%. At present the method is limited to saccharides for which reference samples are available. B. B. BAUMINGER

4511. Determination of aldopentoses in the presence of ketopentoses. A. Bonsignore, G. Vergano and P. Segni (Ist. Chim. Biol., Univ. Genova, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1958, **34** (7), 324–327.— The method of Dische and Borenfreund (*Anal.*

Abstr., 1957, **4**, 4077) is examined. It is pointed out that the absorption max. is at 560 mμ instead of 552 mμ. L. ZANONI

4512. Chromatography of some phosphoric acid esters of sugars. B. N. Stepanenko and A. A. Kuznetsov (Lab. Physiol. Chem., Acad. Sci., Moscow). *Biokhimiya*, 1959, **24** (1), 25–32.—The chromatography of fructose esters in nine different acid - organic solvent - water systems shows that fructose 6-phosphate (**I**) always migrates more rapidly than fructose 1:6-diphosphate (**II**). Attempts are made to discover why **II** has previously been stated to move as fast as or faster than **I** with the same solvents. This can happen if the experiment is stopped too soon or if there are procedural errors, the most important of which is the use of a non-specific developer. Diphenylamine is proposed as a developer; this gives a blue - violet colour with **I** and with fructose, and a pink colour with **II** and with fructose 1-phosphate. The diphenylamine (1 g) is dissolved in conc. H_2SO_4 ($1 \cdot 5$ ml) and made up to 100 ml with glacial acetic acid. The dry chromatograms are sprayed with the developer and heated for 5 min. at 80° to 90°. Some sugar phosphates when used in relatively large amounts give two spots of equal colour intensity with some acid solvents. Treatment of the paper with HCl reduces the amount of ester below the level at which this effect is produced.

K. R. C.

4513. Modified system for paper ionophoresis and chromatography of phosphate esters and organic acids. V. C. Runeckles and G. Krotkov (Queens Univ., Kingston, Ontario, Canada). *Arch. Biochem. Biophys.*, 1959, **80** (1), 94–96.—Improved resolution of the compounds is attained in the method described previously (*Anal. Abstr.*, 1958, **5**, 642) by electrophoresis in $2 \cdot 5$% pyridine in $0 \cdot 25$% aq. acetic acid by applying d.c. at 800 V (20 V per cm). Chromatography in the second dimension is with 2-methoxyethanol - pyridine - glacial acetic acid - water ($8:4:1:1$) containing $0 \cdot 15$% (w/v) of 8-hydroxyquinoline. W. H. C. SHAW

4514. Sensitive and rapid method for the determination of citrates in biological materials. A. P. Safronov. *Biokhimiya*, 1959, **24** (1), 123–126.— Citric acid is oxidised electrolytically to pentabromoacetone, which gives a colour reaction with pyridine and alkali. An apparatus is described. *Procedure*—Into the electrolytic cell introduce 10 to 40 μg of citric acid (not exceeding 4 ml), 20 N H_2SO_4 ($0 \cdot 5$ ml), 8% $MnSO_4$ soln. ($0 \cdot 1$ ml), N KBr ($0 \cdot 2$ ml) and 40% H_3PO_3 soln. ($0 \cdot 25$ ml) and make the vol. up to 5 ml. Pass a current of $0 \cdot 2$ amp. for 10 min. at 3 V. Disconnect and add to the cell 1% H_2O_2 soln. ($0 \cdot 5$ ml) and 12% sulphosalicylic acid soln. ($0 \cdot 2$ ml). Remove the liquid from the cell and wash the cell and its electrode with *iso*octane (6 ml), adding the washings to the main body of liquid; shake the mixture for 1 min. and allow it to settle. Transfer 5 ml of the extract to 30% KOH soln. (2 ml) to which pyridine (4 ml) has been added, shake vigorously and then immerse in a water bath at 80° for 3 to 4 min. A pale-pink to red colour indicates the presence of citric acid. The colour is measured photometrically at 530 mμ. Results for citric acid in blood and urine are quoted. The method is satisfactory for the determination of 10 to 400 μg of citric acid. K. R. C.

4515. Biological assay for gibberellic acid with rice seedlings. R. S. C. Aytoun, A. T. Dunn and D. A. L. Seiler (Glaxo Lab. Ltd., Sefton Park, Stoke Poges, Bucks., England). *Analyst*, 1959, **84**, 216–221.—Rice seedlings (selected from seeds germinated under specified conditions at 28° for 72 hr.) were placed in dishes, specially designed to maintain the plants in an upright position with their roots in the treatment soln. of gibberellic acid in tap water, and the randomised dishes were placed in a polyethylene chamber (humidity >90%) and incubated at 29° to 30° for 72 hr. with an illumination of 6 ft.-candles. Preliminary experiments showed that either the growth in 72 hr. or the difference between that and the growth in 24 hr. gave the best results, and the former was used for convenience. The statistical examination of the results showed that the method is suitable for the quant. bio-assay of gibberellic acid.

A. O. JONES

4516. Determination of "direct" alcohol-precipitable bilirubin. A. Pittera (Ist. Pat. Med. Univ. di Catania, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1958, **34** (14), 710–713.—The "direct" bilirubin is determined at acid pH in aq. soln. (0·5 ml of serum, 0·5 ml of dizao reagent and 4 ml of 0·025 N HCl); after the photometric reading the addition of 1 ml of HCl and 4 ml of 95% ethanol allows the "indirect" bilirubin to react; the total bilirubin is thus obtained. Then 1 ml of 12% Na_2SO_4 soln. is added and, after centrifugation, the ppt. containing the "direct" precipitable bilirubin is removed, and a further spectrophotometric reading is made. From these readings the total, "direct" and "direct" non-alcohol-precipitable bilirubin can be derived.

L. ZANONI

4517. Spectroscopy of bacterial chlorophylls separated by paper and cellulose column chromatography. I. R. Kaplan and H. Silberman (Sydney Univ., Australia). *Arch. Biochem. Biophys.*, 1959, **80** (1), 114–124.—Methods are given for the extraction and purification of bacterial pigments on Whatman 3 MM circular papers developed with toluene and on cellulose powder columns developed with 20% benzene in light petroleum to eliminate carotenoids, then with 0·5% *iso*propyl alcohol in light petroleum to elute chlorophylls. All solvents are saturated with H_2S to prevent oxidation. Visible and u.v. absorption curves of the isolated chlorophylls are given.   W. H. C. SHAW

4518. Rapid colorimetric method for the determination of tocopherol and tocopheryl acetate in plasma. G. Rindi (Univ., Pavia, Italy). *Int. Z. Vitaminforsch.*, 1958, **28**, 225–234.—Total tocopherol in plasma is determined colorimetrically by a modified $FeCl_3$ - 2 : 2'-dipyridyl reaction after alkaline saponification in the presence of ascorbate to prevent oxidation of the tocopherol. Free tocopherol is determined by the same colorimetric reaction on another sample of the plasma. Esterified tocopherol is calculated by difference. A correction is made for interference by carotene.

CHEM. ABSTR.

4519. Enzymic formation of high levels of 1 : 3-diphosphoglycerate from 3-phosphoglycerate : isolation and further metabolism. [Determination of 2 : 3-diphosphoglycerate.] I. Krimsky (Div. of Nutr. and Physiol., Publ. Hlth. Res. Inst. of City of New York Inc., U.S.A.). *J. Biol. Chem.*, 1959, **234** (2), 228–231.—2 : 3-Diphosphoglycerate is measured by its activating effect on the phosphoglycerate

mutase reaction in the conversion of phosphoenol pyruvate into 3-phosphoglycerate, catalysed by enolase and phosphoglycerate mutase. The initial rate of decrease in the absorption at 240 mμ, due to the decrease in phosphoenol pyruvate, is proportional to the concn. of 2 : 3-diphosphoglycerate, when this is present in limiting amounts.

J. N. ASHLEY

4520. Estimation of carbohydrates of the glyco lipids in tissues and body fluids. J. Brückner (Dept. of Path., Med. Sch., Univ. of Otago, Dunedin, N. Zealand). *Clin. Chim. Acta*, 1959, **4** (2), 149–160.—Glycolipids are extracted from pretreated tissues and hydrolysed with acid. The carbohydrate moiety is then determined with orcinol - H_2SO_4 or with Somogyi's copper reagent.

H. F. W. KIRKPATRICK

4521. Determination of volatile fatty acids in bovine blood by isotope dilution. J. B. Holter, S. Lakshmanan and J. C. Shaw (Maryland Univ., College Park, U.S.A.). *J. Dairy Sci.*, 1959, **42** (2), 358–362.—The levels of acetate, butyrate and valerate in various samples of cows' blood are determined by an isotope dilution method with the appropriate ^{14}C-labelled compounds. The acids are steam-distilled and titrated after concentration and chromatographic separation. Counting is carried out on the dry residues from the titrations. Most of the volatile fatty acid was present as acetate, with a little butyrate and little or no valerate.

W. H. C. SHAW

4522. Isolation of salicyluric acid from urine. D. Hostýnová, P. Kovács, R. Dzúrik and T. R. Niederland (Dep. Chem., Pharm. Fac., Komenský Univ., Bratislava). *Farmácia, Bratislava*, 1959, **28** (5), 145–149.—The method of Quick (*J. Biol. Chem.*, 1935, **101**, 475) was modified and its accuracy increased by controlling the course of the isolation by means of paper chromatography. The chromatograms were developed with *n*-butanol - acetic acid - H_2O (10 : 1 : 14) in an atmosphere made alkaline by 0·2% aq. NH_3 on Whatman No. 1 or S. & S. 2043 paper by the descending technique. The separated spots were detected in u.v. light after having been sprayed with a soln. of diazotised *p*-nitroaniline and sulphanilic acid or with 0·2% $FeCl_3$ soln.   J. ZÝKA

4523. Estimation of catecholamines in urine. U. S. von Euler and F. Lishajko (Dept. of Physiol., Karolinska Inst., Stockholm, Sweden). *Acta Physiol. Scand.*, 1959, **45** (2–3), 122–132.—The urine (25 ml) is boiled and filtered, EDTA (disodium salt) (0·5 g) is added, and the pH is adjusted to 8·2 to 8·3 with N NaOH. The treated urine is passed through aluminium oxide (1 g) in a 10-mm-diam. column at a rate of 1 to 2 ml per min., the column is washed with water (10 to 15 ml) at the same rate, and the catecholamines are eluted with 0·25 N acetic acid (2 × 5 ml). The eluate is neutralised to pH 6·2 to 6·3 with N aq. NH_3 and a suitable aliquot is oxidised with 0·25% $K_3Fe(CN)_6$ soln. (0·1 ml). After 2 min. a fresh mixture of 20% NaOH soln. and 2% ascorbic acid soln. (9 : 1) (1·0 ml) is added and the volume is made up to 10 ml with water. (If more than 1 ml of eluate is taken an equal volume of alkali - ascorbic acid soln. is added.) A blank is prepared by adding all the reagents except $K_3Fe(CN)_6$ to an aliquot of the eluate. The fluorescence of sample and blank is measured within 10 min. in a fluorimeter with two sets of filters— (*a*) primary 395-mμ interference filter and secondary

Ilford **623** (490 mμ), (b) primary **436**-mμ interference filter and secondary Corning **3486** (540 mμ). The results are calculated with the aid of the following formulae, where m and n are the observed fluorescence values (sample — blank) with filter sets a and b, respectively, and A_a, A_b, N_a and N_b represent the fluorescence per μg of adrenaline and noradrenaline, respectively, determined at the same sensitivity as for the samples—noradrenaline $= y = [(mA_b/A_a) - n]/(N_a A_b/A_a - N_b)$, adrenaline $= (n - yN_b)/A_b$. A lucite rod can be used as a standard after the determination of its fluorescence in terms of adrenaline and noradrenaline. Recoveries of added catecholamines are 70 to 100%.

R. A. BRENAN

4524. Study of the reaction of adrenaline with ethylenediamine. G. Nadeau and L.-P. Joly (Dept. of Chem., Univ. Laval, Quebec, Canada). *Canad. J. Biochem. Physiol.*, 1959, **37** (2), 231–244 (in French).—Optimum conditions for the reaction are defined. The necessity for a preliminary oxidation to adrenochrome is confirmed. The reaction pH should be 10·4 $\pm$ 0·1 and the extraction of the fluorescent compound is best made with *iso*butyl alcohol. The reacting mixture should contain 114·5 millimoles of ethylenediamine base per 100 ml, and the reaction allowed to proceed for 20 to 30 min. at 50°. Exposure to diffuse or u.v. light affects the yield of fluorescent compound. The beneficial effect of various ions is discussed.

H. F. W. KIRKPATRICK

4525. Determination of adrenaline and noradrenaline. I. Modified reaction with ethylenediamine. G. Nadeau and G. Sobolewski (Hôp. St.-Michel Archange, Quebec, Canada). *Canad. J. Biochem. Physiol.*, 1959, **37** (3), 441–451 (in French).—Treatment with molybdate before the addition of ethylenediamine gives reproducible and enhanced fluorescence. The reaction is carried out at room temp. and at 50°, the difference in the two fluorescence readings being a measure of the noradrenaline, and the room-temp. reading may be corrected to give the adrenaline concn. *Procedure*—To the soln. of amines (10 ml) add 1% aq. ammonium molybdate soln. (0·8 ml), and set aside at room temp. in the dark for 30 min. Add a reagent (0·5 ml) composed of ethylenediamine (60 ml) and azeotropic HCl (30·8 ml), both freshly distilled, diluted to 100 ml with H_2O. Set aside for 30 min. as before, extract with *iso*butyl alcohol (10 ml) and read the fluorescence (F_1) of the organic phase. Return the alcohol to the reaction mixture, heat at 50° for 30 min., cool, shake and again read the fluorescence of the alcohol layer (F_2). Correct F_1 and F_2 by deducting the blank fluorescence. Then adrenaline $(\mu g) = K_1(F_1 - K_2 F_2)$, and noradrenaline $(\mu g) = K_3(F_2 - F_1)$, where K_1, K_2 and K_3 are constants for the apparatus evaluated with known amounts of the amines. H. F. W. KIRKPATRICK

4526. Identification of thyroxamine in thyroid and plasma. G. Hillmann, B. Keil and P. Taslimi (Chem. Lab., Med. Univ.-klinik, Tübingen, Germany). *Z. Naturforsch.*, 1958, **13b**, 820–821.—Butanol extraction of ^{131}I-labelled rat-thyroid homogenates (not hydrolysed) followed by isotopic co-crystallisation with thyroxamine (pptn. from HCl - ethanol soln. with conc. aq. NH_3) separates the thyroxamine from other iodine compounds. Paper chromatography is made with 50% piperidine. Further identification can be afforded by conversion into thyroxamine N-succinate, followed by paper chromatography in *iso*amyl alcohol - 5 N

aq. NH_3 as well as *tert.*-amyl alcohol - 5 N aq. NH_3. The compound is detected by autoradiography.

H. F. W. KIRKPATRICK

4527. Determination of urea by diacetyl monoxime. R. Sardou (Hôpital Purpan, Toulouse, France). *Ann. Biol. Clin.*, 1958, **16**, 53–60.—Urea in either whole blood or serum was determined on a filtrate, deproteinised with alkaline $ZnSO_4$, by treating the filtrate with diacetyl monoxime in the presence of a soln. of arsenic acid in H_2SO_4. A yellow colour (475 mμ) developed after heating for 5 min. A standard curve was necessary because of the non-linearity of the curve, but results were accurate to within $\pm 1\%$ regardless of the type of blood soln. or clotting agent (oxalate or fluoride) used. CHEM. ABSTR.

4528. Applications of isatin in the paper chromatography of amino acids. U. Bonomi and R. Vecchioni (Ist. di Patolog. Gen. dell'Univ. di Siena). *Boll. Soc. Ital. Biol. Sper.*, 1959, **35** (5), 210–211.—Isatin, sprayed on paper chromatograms as a 0·4% soln. in acetone, was used to locate and identify proline, hydroxyproline, phenylalanine, histidine, asparagine, aspartic acid, cysteine, glycine, cysteic acid, glutamic acid, methionine, norvaline and tryptophan. A minimum of $\simeq 2$ μg of any amino acid was detectable by the spray. Individual amino acids yielded characteristic colours, which developed on paper within 5 to 24 hr., but (except with proline and phenylalanine) not when the reactants were mixed in solution. C. RAINBOW

4529. Technique of separation of amino acids on ion-exchange columns. J. Schormüller, H.-D. Belitz and G. Adler (Inst. f. Lebensmittelchem. u. Lebensmitteltechnol., Berlin). *Z. Lebensmitt-Untersuch.*, 1959, **109** (2), 129–134.—The procedure is based, with modifications, on the Moore and Stein technique. A soln. (1 to 2 ml at pH 2·5) of the acids (5 to 15 mg) is deposited on a suitably prepared column (125 cm high) of Dowex 50-X8 resin which has previously been washed with a citrate buffer at pH 3·1. The first elution is carried out with this buffer at 37·5°, and the second with a citrate buffer at pH 4·25 at temp. gradually rising to 60°. A succession of the acid and neutral amino acids is thus eluted in 1- or 2-ml portions. To separate the basic acids, a separate soln. (at pH 4·0) is added to a 20-cm column (previously washed with a citrate buffer at pH 5·0), the acid and neutral amino acids are washed out with a citrate buffer at pH 5·0, after which the basic acids are progressively eluted at room temp. with a phosphate buffer at pH 6·9 followed by a citrate buffer at pH 6·5. The individual acids in the eluates are determined spectrophotometrically with the use of the Moore and Stein (modified) ninhydrin reagent. The use of a buffer at pH 3·1 on the first column improves the separation of glycine and alanine. The overlapping of proline and glutamic acid in their respective eluates can be resolved by carrying out the optical determination with two different light filters. The peak positions for the basic acids differ slightly from those given by Moore and Stein. The max. error of the individual determinations is $\not> 7\%$. P. S. ARUP

4530. Determination of amino acids in keratin. The content of alanine, glycine, serine and threonine in horn. J. Mareček (Res. Inst. Fats and Oils, Prague). *Chem. Listy*, 1959, **53** (2), 194–196.—Hydrolyse the sample (100 g) by boiling with HCl

(20%) (300 ml) under reflux for 24 hr., evaporate to a syrup, dilute with H_2O, filter and wash the residue. Dilute the combined filtrate and washings to 500 ml. The determination of amino acids can be carried out (i), by measuring the transmittance (Pulfrich photometer) of a methanolic soln. of the stabilised spots eluted from chromatograms after triple development by one-dimensional chromatography on Whatman No. 1 paper with butanol - acetic acid - water (4 : 1 : 5) and comparison with a calibration curve, (ii), by the method of descending standard and ascending sample or (iii) by the titration method of Virtanen et al. (Hoppe-Seyl. Z., 1940, **193**, 268) for the determination of acet-aldehyde formed from alanine by reaction with ninhydrin. Satisfactory agreement was found between the three methods. J. ZÝKA

4531. Rapid quantitative determination of arginine, histidine and lysine by ion-exchange paper chromatography. H. R. Roberts and M. G. Kolor (Nat. Dairy Products Corp., Oakdale, N.Y., U.S.A.). Anal. Chem., 1959, **31** (4, Part I), 565–566.—The qualitative technique of Tuckerman (cf. Anal. Abstr., 1958, **5**, 2338) was made quantitative. A 4-hr. descending development with an acetate buffer (pH 5·2) resolves these compounds as round compact spots, the maximum densities of which are linearly related to the log. of the concn. The standard deviation was $< \pm 1.5\%$. G. P. COOK

4532. Microchemical determination of histidine in protein hydrolysates and urine. K. Voigt (Inst. for Med. and Biol., Acad. of Nat. Sci., Berlin). Biochem. Z., 1959, **331** (2), 127–132.—The method described is a modification of that of Kapeller-Adler (Biochem. Z., 1933, **264**, 131; 1934, **271**, 206), in which histidine is treated with bromine in acetic acid soln. and, on the addition of an aq. NH_3 - ammonium acetate or an aq. NH_3 - ammonium chloride buffer, a blue or blue - violet colour, respectively, is produced. These colours, which follow Beer's law, are measured photometrically. The blue colour is the more sensitive to changes in histidine concn., and 0·2 to 0·7 mg of histidine can be determined. Cyclic amino acids, methionine, indolylacetic acid, uric acid, phenol, heavy-metal salts and excess of bromine affect the intensity and quality of the colour produced. In the application of the method to protein hydrolysates and urine, impurities are first removed by treatment with H_2S, followed by passage of the soln. through columns of activated charcoal and Wofatit C. For urine it is necessary to pre-treat with Pb acetate, before passage of the H_2S. Results are given for the histidine content of normal urine (29 to 65 mg per 24 hr.), and of urine from malignant tumour cases (0 to 63 mg per 24 hr.), also for serum albumin (human), serum globulin (rat), and hydrolysates from experimental tumours in mice and rats. D. B. PALMER

4533. New method of determination of mercapto groups in biological preparations. A. Mussini (Ist. Farmacol., Univ. of Milano, Italy). Boll. Soc. Ital. Biol. Sper., 1958, **34** (21), 1419–1421.—Procedure—The sample (≡ 1 to 4 μg of –SH) is triturated with a mixture of EDTA and sulphosalicylic acid (1·25 ml of 0·335% EDTA soln. plus 1·25 ml of 2·5% sulphosalicylic acid soln.). The mixture is centrifuged and to an aliquot of the supernatant liquid (0·25 ml to 1 ml) is added 2 ml of p-chloromercuri-benzoic acid soln. (0·001%), with shaking, followed by 25 ml of 0·3 N acetic acid and 1 ml of dithizone

reagent (100 mg of dithizone in 100 ml of $CHCl_3$; 3 ml of this soln. is diluted to 90 ml with $CHCl_3$). After shaking, the $CHCl_3$ layer is made up to 10 ml and the extinction is read at 620 mμ. L. ZANONI

4534. Colorimetric determination of cysteine. H. F. Liddell and B. Saville (Chem. Defence Exp. Estab., Porton Down, Salisbury, Wilts., England). Analyst, 1959, **84**, 188–190.—To prepare a calibration graph, soln. of cysteine hydrochloride (L or DL form) containing 1 to 70 μg per ml are made. To a 1-ml portion of each of these are added 5 ml of a soln. of HNO_3 (5 ml of 0·01 M aq. $NaNO_2$ added to 40 ml of H_2SO_4 and diluted to 100 ml) and, after 5 min., 1 ml of a 0·5% soln of ammonium sulphamate and then ≃ 10 ml of a soln. prepared by mixing 4 vol. of a 3·44% soln. of sulphanilamide in 0·4 N HCl with 1 vol. of a 1% soln. of $HgCl_2$ in 0·4 N HCl. Finally the liquid is diluted to 25 ml with a 0·1% soln. of N-1-naphthylethylenediamine dihydrochloride in 0·4 N HCl and the extinction is measured absorptiometrically with Ilford No. 605 filters. The sample soln. is treated similarly. A simplified procedure is described in which the last two soln. are added as a mixture, the loss of accuracy being slight. The reaction is specific for mercapto groups. There is no interference from Zn, but I⁻ and extremely large amounts of Hg, Ag and Cu²⁺ interfere. A. O. JONES

4535. Estimation of cysteine and cystine at the mercury-pool electrode. R. C. Kapoor (Univ. Allahabad, India). Z. anal. Chem., 1959, **166** (1), 1–4 (in English).—The amperometric titration of cysteine and cystine in concn. of 10^{-3} M with phenylmercury chloride and with $HgCl_2$ was studied with a mercury-pool electrode. The titrations were conducted under nitrogen in soln. buffered to pH 5 and pH 9·2 in the presence of KCl (0·1 M and 2·0 M) and, for cystine, Na_2SO_3 (0·01 M). Polarograms were recorded manually and automatically. G. BURGER

4536. Determination of β-lipoproteins of serum with calcium chloride and heparin. M. Greppi, F. M. Antonini and C. Salvini (Ist. Chim. Med. Gen., Univ., Firenze, Italy). Boll. Soc. Ital. Biol. Sper., 1958, **34** (20), 1339–1343.—The method described is based on the measurement of the turbidity formed by serum in the presence of calcium chloride on the addition of heparin. Procedure—Serum (1 ml) containing 10% of $CaCl_2$ is diluted with 10 ml of heparin soln. (1%). The reading is carried out at 700 mμ 20 min. after the addition of heparin. The mean error is ± 0·67%. L. ZANONI

4537. New method for photometric determination of small amounts of protein. W. Heinzel and V. Neuhoff (Path. Inst. d. Univ., Tübingen, Germany). Naturwissenschaften, 1959, **46** (4), 146.—The test soln. is spotted on to poly(vinyl chloride) paper ("Rhovyl," S. & S.) previously impregnated with oleic acid, dried and stained with Amido black 10B (C.I. Acid Black 1), as in electrophoresis. The paper is transferred to a glass cell containing just sufficient nitrobenzene to render it transparent, and the extinction is read at 610 mμ in a specially adapted spectrophotometer. H. F. W. KIRKPATRICK

4538. Sources of error in the paper-electrophoretic determination of serum glycoproteins. W. Boguth and H. Schnappauf (Vet.-Physiol. Inst. d. Justus Liebig Univ., Giessen, Germany). Naturwissenschaften, 1959, **46** (4), 145–146.—Two main sources

of error are noted. Albumin is lost by elution into reagents owing to insufficient fixing, and an error in scanning is introduced by the use of a transparency oil of unsuitable refractive index. To eliminate these errors, the drying temp. of the strip should be 150°, and the refractive index of the oil used for rendering it transparent should be 1·55.

H. F. W. KIRKPATRICK

4539. Albumin trail in paper protein electrophoresis. W. B. Yeoman (Frenchay Hosp., Bristol, England). *Clin. Chim. Acta*, 1959, **4** (2), 246–251.— The trail of albumin on Whatman No. 1 paper is of the order of 9 to 14% if 0·01 ml of serum is used. The correction may be conveniently assessed in electropherograms by drawing a line parallel to the abscissa of scan at a height above the abscissa equal to one-third of the height of the minimal trough shown by the scan. All of the area between this line and the abscissa is considered as albumin.

H. F. W. KIRKPATRICK

4540. Staining properties of Oil Red O and a method of partial purification of the commercial product. H. Kutt and T. T. Tsaltas (Neurol. Service of the Cornell Med. Div., Bellevue Hosp., New York, U.S.A.). *Clin. Chem.*, 1959, **5** (2), 149–160.—A yellow - brown constituent of commercial Oil Red O (C.I. Solvent Red 27) stains serum proteins so that lipid electropherograms consist of a red lipid pattern superimposed on a brownish protein pattern. Successive treatments of the dye with 60% ethanol by refluxing, cooling and decantation yield a residue consisting principally of a red constituent that moves slowly on paper chromatograms developed with 95% ethanol. This partial purification yields a dye that stains lipoproteins satisfactorily.

H. F. W. KIRKPATRICK

4541. Chromatography of proteins. III. Human, horse and dog haemoglobins on cation-exchange cellulose. F. J. Gulter, E. A. Peterson and H. A. Sober (Nat. Cancer Inst., U.S. Dept. Health, Bethesda, Md., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **80** (2), 353–366.—Chromatography of haemoglobins in the carboxy form is carried out on carboxymethylcellulose eluted with $0.01 M$ sodium phosphate buffers to give a gradient of increasing pH. Eluted fractions are examined spectroscopically, and, after concentration, by paper electrophoresis and sedimentation methods. The heterogeneous nature of adult human and horse carboxyhaemoglobins and the effects of temp. and of conc. urea soln. on the chromatography are discussed.

W. H. C. SHAW

4542. Ferrous iron - sulphuric acid reagent for the determination of pure oestrogens. E. Epstein, W. O. Maddock and A. J. Boyle (Dept. of Chem. and Med., Wayne State Univ., Detroit, Mich., U.S.A.). *Talanta*, 1959, **2** (2), 183–186.—For the determination of oestrone (**I**) and oestradiol (**II**), measured amounts of soln. are evaporated on a water bath in round Coleman spectrophotometer cells (19 mm × 150 mm). The reagent [290 mg of $(NH_4)_2SO_4.FeSO_4.6H_2O$ (**III**) in 100 ml of 52% H_2SO_4; stable for 3 days if protected from air] (8 ml) is added, the mixtures are heated in a boiling-water bath (50 min. for **I**, or 30 min. for **II**), then cooled and read at 505 mμ. For the determination of oestriol (**IV**), the soln. is evaporated as described above, then treated with 8 ml of reagent (290 mg of **III** dissolved in 7·5 ml of water and made up to 100 ml at room temp. with 70% H_2SO_4), heated as described above for 50 min., then cooled and read at 500 mμ. Results are referred to the appropriate

standard curves, which are linear up to 17·5 μg (for **I** and **II**) or 33 μg (for **IV**). The reproducibility ranges are from 3 to 9% (for **I**), 5 to 8% (for **II**) and 1 to 5% (for **IV**).

R. E. ESSERY

4543. Two-dimensional chromatography, electrophoresis and electrochromatography of ketosteroids. P. Bianchini and M. Mantovani (Lab. Ric. Crinos Ind. Farmacol., Milano, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1958, **34** (18), 1106–1110.—In the two-dimensional chromatographic method described, butanol - methanol - benzene - H_2O (1:1:1:1) is used as developer. The electrophoresis is carried out with a borate buffer at pH 8·6 at 150 to 360 V for 7 to 20 hr. The detection is made with K_2PtI_6, aniline phthalate or hexamethylenediamine. In a combination of these methods, chromatography is carried out on paper (30 cm × 30 cm) with the starting point on the middle line of the paper; after development and drying, the chromatogram is submitted to electrophoresis after folding it along the middle line. With this technique excellent separation of ketosteroids can be attained.

L. ZANONI

4544. Estimation of corticosteroids by the reduction of ferricyanide. N. R. Stephenson (Lab. of the Food and Drug Directorate, Dept. of Nat. Health and Welfare, Ottawa, Canada). *Canad. J. Biochem. Physiol.*, 1959, **37** (3), 391–398.—The α-ketolic side-chains of the adrenal corticosteroids are susceptible to oxidation, and in this method the ferrocyanide produced by the reduction of alkaline ferricyanide is measured photometrically as Prussian blue. Dissolve the steroid in aldehyde-free 95% ethanol and add 0·5 ml of the soln. to 0·1% $K_3Fe(CN)_6$ soln. (0·5 ml) in a 10-ml glass stoppered graduated cylinder. Add 0·23% Na_2CO_3 soln. (1·0 ml), stopper the cylinder and immerse it to a depth of approx. 4 cm in a 60° constant-temp. water bath for exactly 60 min. Cool the cylinder in water at 15° for 1 to 2 min., add 0·2% $(NH_4)_2SO_4.Fe_2(SO_4)_3.12H_2O$ soln. containing 5·5% of 85% H_3PO_4 (1·0 ml) and mix by gentle swirling. Allow the colour to develop for 15 min. and then dilute the reaction mixture with water to 6·0 or 10·0 ml according to the amount of steroid present. Measure the extinction of test and reagent blank (0·5 ml of aldehyde-free 95% ethanol treated as described above) at 620 mμ. Beer's law is obeyed over the range 0·005 to 0·050 mg of steroid. The relative reducing activities of several corticosteroids are compared.

R. A. BRENAN

4545. Determination of the activity of starch hydrolysing enzymes. M. Richter (Inst. Ernährung, Potsdam-Rehbrücke, Berlin, Germany). *Ernährungsforschung*, 1959, **4** (1), 19–34.—Three methods depending on (*i*) the change in viscosity, (*ii*) the iodine colour, and (*iii*) the reducing power, are reviewed. Newer views on the kinetics of enzymic breakdown are discussed. (49 references.)

S.C.I. ABSTR.

4546. Simple method for the assay of carbohydrases. R. W. P. Master (Haffkine Inst., Parel, Bombay, India). *Experientia*, 1959, **15** (3), 123–124 (in English).—Carbohydrate soln. (10%) (1 ml) is mixed with a dialysed enzyme preparation (1 ml) and buffer soln. of the appropriate pH. The mixture is incubated at 37° for 24 hr. Aliquots (10 μl) of the reaction mixture, together with standard sugar soln., are applied to points on the circumference of a circle (3·0 cm diam.) drawn at the

centre of a filter-paper disc. By using appropriate chromatographic solvents and chromogenic locating reagents, the products of the enzyme reaction are then determined. The method, which gives reasonably accurate results when quick determinations are required, is most convenient when the products of the reaction have R_F values very different from those of the substrates.   P. Nicholls

4547. Electrophoretic behaviour of serum amylase. [Determination of amylase.] R. L. McGeachin and J. P. Lewis (Dept. of Biochem., Univ. of Louisville Sch. of Med., Ky., U.S.A.). *J. Biol. Chem.*, 1959, **234** (4), 795–798.—The amyloclastic amylase determination of Van Loon *et al.* (*Amer. J. Clin. Path.*, 1952, **22**, 1134) has been modified for use on the micro scale. The quantities of samples and reagents are reduced to 10% of the original amounts and barbitone buffer, pH 7·6, is used instead of phosphate buffer, pH 7·0, in some comparative determinations. The extinctions of the blue starch-iodine mixtures are determined spectrophotometrically at 660 mμ.   J. N. Ashley

4548. New method of demonstrating esterases in skin. G. K. Steigleder and H. Elschner (Univ.-Hautklinik, Frankfurt am Main, Germany). *Klin. Wochschr.*, 1959, **37** (2), 104–105.—A reagent that will demonstrate esterases on the surface of living skin and in sections by the production of a grey-blue colour which changes to black consists of 0·1% (w/v) 1-naphthyl acetate and 0·1% (w/v) Fast blue salt BB (C.I. Azoic Diazo Component 20), both dissolved in a few drops of acetone, in 0·1 M phosphate buffer. In the control soln. 1-naphthol replaces the 1-naphthyl acetate. For living skin, the soln. is placed in a small glass cell affixed to the selected site with adhesive tape. The reaction is complete after 25 min.   D. B. Palmer

4549. Spectrophotometric method for determination of diamine oxidase (DAO) activity. B. Holmstedt and R. Tham (Dept. of Pharmacol., Karolinska Inst., Stockholm 60, Sweden). *Acta Physiol. Scand.*, 1959, **45** (2–3), 152–163.—Diamino compounds are oxidised by diamine oxidase to the corresponding aminoaldehydes. If butane-1:4-diamine dihydrochloride (putrescine) is used as the substrate, the aldehyde formed condenses to the cyclic compound $\triangle^1$-pyrroline, and this will react with *o*-aminobenzaldehyde to give a yellow compound, probably 1:2-dihydro-2:3-trimethylenequinazolinium hydroxide. The enzyme preparation, in phosphate buffer $M/15$, pH 6·8, is added to 0·005 M *o*-aminobenzaldehyde, also in phosphate buffer (2·5 ml) and the volume is made up to 4·5 ml with the buffer. After temperature equilibration, 0·1 M putrescine in phosphate buffer (0·5 ml) is added and the mixture is incubated at 37°, usually for 3 hr. The reaction is stopped by the addition of 10% trichloroacetic acid (1·0 ml), and after centrifugation the extinction of the supernatant liquid is measured at 430 mμ. A blank is prepared by carrying out this procedure, but omitting the addition of putrescine.   R. A. Brenan

4550. Purification and properties of glutathione peroxidase of erythrocytes. [Determination of glutathione peroxidase activity.] G. C. Mills (Dept. of Biochem., Univ. of Texas Med. Branch, Galveston, U.S.A.). *J. Biol. Chem.*, 1959, **234** (3), 502–506.—Two methods of assay are described. In the first method the ability of the peroxidase-reduced glutathione system to prevent the oxidative

breakdown of haemoglobin is used as a measure of the enzymic activity. The choleglobin formed from haemoglobin is determined by a standard method. In the second method the rate of oxidation of reduced glutathione by H_2O_2 is used as a measure of the peroxidase activity. The peroxidase catalyses the reduction of H_2O_2, with reduced glutathione serving as H donor. Reduced glutathione, which is left at the end of the reaction, is determined by the mercuribenzoate method of Boyer (*J. Amer. Chem. Soc.*, 1954, **76**, 4331).   J. N. Ashley

4551. Assay of arylsulphatases A and B in human urine. H. Baum, K. S. Dodgson and B. Spencer (Dept. of Biochem., Univ. of Wales, Cardiff). *Clin. Chim. Acta*, 1959, **4** (3), 453–455.—The determination of these enzymes independently in the presence of each other is possible from the following observations. Normal kinetics are shown by A at low substrate concn. in the presence of $2·5 \times 10^{-4}$ M $Na_4P_2O_7$, whilst considerable inhibition of B occurs under these conditions. B is specifically inhibited by Cl⁻ when potassium 2-hydroxy-5-nitrophenyl sulphate is the substrate, whereas A is not. The determination of B in the presence of A is based on the observation of only a small residual activity after the first 20 min. of reaction on incubation at high substrate concn. in the presence of Ba^{2+} and in the absence of interfering ions. Practical details are given.
    H. F. W. Kirkpatrick

4552. Simple micro-method for the determination of uropepsin in urine. R. Ménaché (Lab. Clin. de l'Hôpital "Hasharon," Petah-Tikva, Israel). *Bull. Soc. Chim. Biol.*, 1959, **41** (1), 175–180.—The tyrosine produced by the incubation of 0·2 ml of urine with a haemoglobin substrate for 1 hr. at 37° and pH 1·5 to 2·5 is measured colorimetrically by its reaction with Folin and Ciocalteu's phenol reagent. Tyrosine standards are used for comparison, and the results are expressed as the tyrosine (mg) which would be produced by the 24-hr. urine output. Normal values (for Israel) are taken as 300 to 600 mg of tyrosine per 24 hr.; 3 determinations on the same urine gave values of 440, 470 and 430 mg per 24 hr.
    D. W. Moss

4553. Simple colorimetric method for estimating serum pseudocholinesterase. R. L. Smith, H. Loewenthal, H. Lehmann and E. Ryan (Chase Farm Hosp., Enfield, Middx., England). *Clin. Chim. Acta*, 1959, **4** (3), 384–390.—The serum is incubated with a buffered phenyl benzoate substrate (pH 8·6) and the liberated phenol is determined with Folin and Ciocalteu's reagent.
    H. F. W. Kirkpatrick

4554. [Determination of] the distribution of glutamic-γ-aminobutyric transaminase in the nervous system of the rhesus monkey. R. A. Salvador and R. W. Albers (Lab. of Neurochem., Nat. Inst. of Neurol. Diseases and Blindness, Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1959, **234** (4), 922–925.—The transaminase activity is determined by fluorimetric measurement of the condensation product of succinaldehydic acid (produced from Na γ-aminobutyrate during incubation with the enzyme) with 3:5-dinitrobenzoic acid. Conditions are described which allow measurement of activity on 3 to 15 μg of lyophilised brain tissue.   J. N. Ashley

4555. [Determination of] a bacterial pterin deaminase. B. Levenberg and O. Hayaishi (Nat. Inst. of Arthritis and Metabol. Diseases, Bethesda,

Md., U.S.A.). *J. Biol. Chem.*, 1959, **234** (4), 955–961.—A spectrophotometric method is described, based on shifts in the u.v. spectrum of 2-amino-4-hydroxypteridine-6-carboxylic acid which accompany the conversion of the 2-amino group into the 2-hydroxy group by the deaminase at pH 6·3. The extinction, which is determined at 360 mμ for crude enzyme prep. and at 290 mμ for purer prep., is linearly related to the activity of the enzyme.

J. N. ASHLEY

4556. Nephelometric determination of elastase activity and method for elastoproteolytic measurements. I. Banga, J. Baló and M. Horváth (First Dept. of Path. Anat. and Exp. Cancer Res., Med. Univ., Budapest, Hungary). *Biochem. J.*, 1959, **71** (3), 544–551.—Methods for the determination of elastase activity are reviewed. A rapid and, within certain limits, sufficiently accurate nephelometric method is described in which a photometer is used to measure the changes in extinction of a suspension of elastin granules in the presence of elastase. The extinction is read with a red RG$_1$ colour filter with max. transmission at 620 to 750 mμ, and the amount of enzyme is ascertained from a standard graph.

J. N. ASHLEY

4557. Pyridine nucleotide transhydrogenase. VII. Determination of the reactions with coenzyme analogues in mammalian tissues. [Assay of transhydrogenase activity.] A. M. Stein, N. O. Kaplan and M. M. Ciotti (Graduate Dept. of Biochem., Brandeis Univ., Waltham, Mass., U.S.A.). *J. Biol. Chem.*, 1959, **234** (4), 979–986.—The method, which involves the transfer of hydrogen or electrons from reduced triphosphopyridine nucleotide to the acetylpyridine analogue of diphosphopyridine nucleotide, gives values for transhydrogenase activity much higher than those obtained by other methods. The reaction is carried out at pH 6·5 and 25°, and the activity of the enzyme is determined from the amount of the acetylpyridine analogue of reduced diphosphopyridine nucleotide; this is measured spectrophotometrically at 365 mμ.

J. N. ASHLEY

4558. Assay of pepsin using ribonuclease as substrate. A. Berger, H. Neumann and M. Sela (Weizmann Inst. Sci., Rehovoth, Israel). *Biochim. Biophys. Acta*, 1959, **33** (1), 249–251.—In the method described, a soln. of the sample pepsin is allowed to react at pH 1·7 with ribonuclease for 30 min. at 25°. The reaction is then stopped by the addition of acetate buffer at pH 7, and the residual ribonuclease is determined by the addition of ribonucleic acid, adjustment to pH 5 and incubation at 25° for 25 min. Uranyl acetate in 25% HClO$_4$ is added and the extinction of the supernatant liquid obtained by centrifugation is measured at 260 mμ. The graph of extinction *vs.* concn. of pepsin is rectilinear up to 15 μg of sample.

W. H. C. SHAW

4559. Paper-chromatographic assay for ribonucleases using cyclic mononucleotides as substrates. J. T. Nodes (Chester Beatty Res. Inst., Royal Cancer Hosp., London, England). *Biochim. Biophys. Acta*, 1959, **32** (2), 551–553.—In the method described, the solution (0·1 ml) is added to 0·1 M acetate buffer at pH 6·0 (0·1 ml) with 0·1 ml of a solution of adenosine (or cytidine) 2′:3′-cyclic phosphate (15 mg per ml) as substrate. After incubation at 37° for 45 min. or 120 min. for the respective substrates, the reaction is stopped with 0·6 ml of ethanol - diethyl ether - CHCl$_3$ (2:2:1). After evaporation to about 0·4 ml during 10 min.

at 85°, portions of the supernatant liquid are applied to Whatman No. 1 paper and developed by the descending technique for 16 hr. with satd. (NH$_4$)$_2$SO$_4$ soln. - *iso*propyl alcohol - M Na acetate (40:1:10). Areas corresponding to the unaltered 2′:3′-cyclic phosphate and to the 2′- and 3′-phosphates are cut out and eluted with 5 ml of water, and the extinctions are measured at 260 mμ (adenosine) or 270 mμ (cytidine). The proportion of substrate hydrolysed is then calculated from the extinctions.

W. H. C. SHAW

See also Abstracts—**4276**, Determination of K and Na in tissues. **4291**, Determination of Be in urine and bone. **4396**, Determination of F in bone. **4446**, Determination of acetyl groups in steroids. **4459**, Separation of isomaltose and gentiobiose. **4562**, Separation of alkaloids from urine, etc. **4567**, Determination of flavonoids in tobacco. **4569**, Determination of curcumin. **4641**, Electrode for intra-vascular O determination. **4652**, Source of error in counting ^{14}C.

Pharmaceutical analysis

4560. Determination of water in drugs containing volatile oils by means of the Karl Fischer method. M. Šaršúnová, Ĺ. Čičmancová and J. Menkynová (Control Pharm. Lab., Bratislava, Czechoslovakia). *Farmácia, Bratislava*, 1959, **28** (2), 55–57.—The Karl Fischer method is recommended for the determination of water in various drugs of the Czechoslovak Pharmacopoeia containing volatile oils, since it avoids the errors caused in usual procedures by drying the material at 100° to 105°. The water in the sample is extracted into abs. methanol by stirring for 5 min. in a closed vessel, and is then titrated in the usual way.

J. ZÝKA

4561. Study of the cation-exchange properties of bentonite with application to the assay of pharmaceuticals. W. G. Gorman and E. P. Guth (Ohio State Univ., Coll. of Pharm., Columbus). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (1), 21–26.—An acid-activated fraction of bentonite was exchange-saturated with gentian violet. This complex was used for a study of exchange reactions with organic cations. The amount of dye released from the complex, measured absorptiometrically, is a function of the concn. of organic cations in soln. and could form the basis for their assay.

A. R. ROGERS

4562. Toxicological investigations of micro quantities of alkaloids by ring paper chromatography. Swarup Narain Tewari and Dharam Narain Tripathi (Clin. Lab., The Mall, Kanpur, India). *Z. anal. Chem.*, 1959, **166** (5), 357–358 (in English). —The separation of various alkaloids extracted in alkaline soln. from viscera, vomit, stomach washes and urine is carried out by circular paper chromatography. A drop of the alkaloid dissolved in dil. acetic acid is placed at the centre of the filter disc (Whatman No. 1, 18 cm diam.) and the wick carrying the solvent (*n*-butanol - acetic acid - water) (5:1:2) is applied below the centre of the filter-paper. The whole system is kept in a glass chamber saturated with the solvent vapours at 20°. The paper is dried after 30 min. Quinine, quinidine, cinchonidine and papaverine are detected by fluorescence, while other alkaloids are detected by the fluorescence-quenching technique of Holiday

and Johnson (*Nature*, 1949, **163**, 216). The spots are revealed by spraying with a modified Dragendorff soln. [0·85 g of $Bi(NO_3)_3$, 10 ml of acetic acid and 40 ml of H_2O mixed with 8 g of KI in 20 ml of H_2O]; for spraying, 10 ml of this soln. is diluted with 5 ml of acetic acid and 25 ml of H_2O. This reagent produces a variety of shades of orange and red with various compounds.   B. B. BAUMINGER

4563. Determination of the quinine content of quinetum, totaquine, liquid extract of cinchona and cinchona bark with the aid of ion-exchange resin. W. Kamp and J. A. Fresen (Rijksuniv., Utrecht). *Pharm. Weekbl.*, 1959, **94** (2), 33–39.—The total alkaloids are isolated from the sample by chromatography on an ion-exchange column (Dowex 50-X2) (H or OH form) and converted into a neutral soln. of the sulphates. This soln. is added to a column of strong anion exchanger (Dowex 1-X2) (chromate form) and left for 12 hr. All the alkaloids except quinine are then eluted with H_2O and the quinine is recovered by elution with either N aq. NH_3 or N formic acid in 96% ethanol. The quinine can then be determined bromimetrically.
G. BURGER

4564. Reactions for the detection of cytisine in forensic studies. I. A. Marenich. *Ukr. Khim. Zhur.*, 1958, **24** (3), 388–390; *Trudy Khar'kovsk. Farmatsevt. Inst.*, 1957, (1), 119–122; *Ref. Zhur. Khim.*, 1959, (1), Abstr. No. 1045.—The crystalloscopic reactions of cytisine (**I**) with the usual pptg. reagents are studied and the optical constants of the resulting crystals are determined. **I** forms hexagonal crystals with a soln. of $KBiI_4$, dendrites with a soln. of Br in NaBr soln., and clusters of needles with a 5% aq. soln. of H_2PtCl_6. The sensitivities of the reactions are 0·3, 1 and 3 μg, respectively. The optical constants of the sublimed crystals of the base **I**, obtained as prisms by the sublimation of **I** by Eder's method at 63° and 1 atm., or at 41° and 3 mm, are determined. The sensitivity of the detection is 0·9 μg. It is found that **I** may be distinguished crystallo-optically from atropine, which reacts analogously to **I** with a soln. of Br in NaBr soln.; certain constants of the compounds of atropine with this reagent are studied. A method is proposed for the detection of **I** in biological material in forensic investigations.
C. D. KOPKIN

4565. The behaviour of some volatile *Nicotiana* alkaloids on distillation and their quantitative determination. C. Pyriki and R. Müller (Inst. f. Tabakforsch., Dresden). *Pharm. Zentralh.*, 1959, **98** (1), 7–19.—Distillation with MgO and steam-distillation with NaOH may be used to separate small quantities of nornicotine, but not of anabasine, from an excess of nicotine. To determine larger quantities of nornicotine, the method of Cundiff and Markunas (*cf. Anal. Abstr.*, 1956, **3**, 814) is recommended. The recovery of total alkaloids by steam-distillation depends on the volume and alkalinity of the soln. distilled.
A. R. ROGERS

4566. Microchemical detection of anabasine and its differentiation from nicotyrine and nicotine. G. Sandri (Ist. di Chim. Agrar. dell'Univ., Bologna). *Mikrochim. Acta*, 1959, (2), 221–229 (in German).—Anabasine gives characteristic crystals with $HBiBr_4$, $HBiI_4$, $HAuBr_4$ and H_2PtBr_6; $CdBr_2$ is used as a reagent for the crystallographic differentiation of nicotine and nicotyrine; and $Co(SCN)_2$ forms with nicotine characteristic pink (hydrated) and blue (anhydrous) crystals.   B. B. BAUMINGER

4567. Method for the determination of the flavonoids in tobacco. M. K. Mikhailov (Hochsch. f. Nahrungs-u. Genussmittelind. Plovdiv, Bulgaria). *Compt. Rend. Acad. Bulg. Sci.*, 1958, **11** (6), 493–496 (in German).—The method is based on the measurement of the yellow colour given by the flavonoids with $AlCl_3$. The flavonoids are extracted into $CHCl_3$ and then into ethanol, and a portion is treated with $AlCl_3$ and K acetate. The colour is measured in a Pulfrich photometer with the S42 filter. Results are reproducible to within about 5%, and agreed to within $\simeq 20\%$ with those obtained by another method. Good results were also obtained by aq. extraction of the tobacco.
G. P. COOK

4568. Paper-chromatographic detection of theophylline and its water-soluble derivatives in pharmaceutical preparations. H. R. Hegi (Kantonsapotheke, Zürich, Switzerland). *Pharm. Acta Helv.*, 1959, **34** (2), 105–109.—Descending chromatography on Whatman No. 1 paper with the upper layer of a mixture of n-butanol - 2 N aq. NH_3 (7 : 3) as mobile phase is used for the separation of 100 to 400-μg quantities of theophylline-7-acetic acid, theophylline, and the dihydroxypropyl, hydroxyethyl and hydroxypropyl derivatives of theophylline. The R_F values are 0·10, 0·30, 0·51, 0·65 and 0·71, respectively. Colour reactions with diazotised sulphanilic acid and diazotised 4-benzamido-2:5-diethoxyaniline (Fast blue salt BB) (C.I. Azoic Diazo Component 20) and the murexide test are used for detection.   A. R. ROGERS

4569. Determination of curcumin in drugs. K. H. Müller and H. Honerlagen (Pharm.-Sci. Section II, A. Natterman and Co., Köln-Braunsfeld). *Arzneimittel-Forsch.*, 1959, **9** (2), 134.—The photometric method described is based on the formation of rubrocurcumin, a 1 : 1 : 1 complex of curcumin, boric acid and oxalic acid. *Procedure*—Heat 100 mg of finely powdered sample with 60 ml of acetic acid for 1 hr. at 90°, add 2 g of boric acid and 2 g of oxalic acid and heat for 10 min. Cool to room temp. and dilute to 100 ml with acetic acid. Dilute a 5-ml aliquot to 50 ml with acetic acid and read the extinction at 540 mμ.   A. G. COOPER

4570. Method for the assay of insulin by paper chromatography. E. L. Fenton (Wellcome Res. Lab., Biol. Div., Langley Court, Beckenham, Kent, England). *Biochem. J.*, 1959, **71** (3), 507–513.—Insulin is separated from impurities and inactive material by ascending chromatography with the upper phase of *sec.*-butyl alcohol and 1% acetic acid (1 : 1, v/v). A soln. of bromocresol green buffered with Na acetate is used to locate the insulin zones. There is a linear relationship between the amount of insulin in the zone and the biological potency of the sample. By elution of the dye from the specific insulin spot and quant. colorimetric comparison with the similar zone from a standard of known potency, the biological potency of the sample can be determined. There is close agreement between the mouse-convulsion method and the chromatographic assay. The potency ratio of a single observation each on test and standard has a coeff. of variation of $\pm 4\cdot3\%$.   J. N. ASHLEY

4571. Colorimetric estimation of penicillamine. Prabhat R. Pal (Dept. of Biol. Chem., Univ. of Michigan, Ann Arbor, U.S.A.). *J. Biol. Chem.*, 1959, **234** (3), 618–619.—A photometric method is described which depends on measurement of the

blue colour formed when penicillamine is heated with $FeCl_3$ and KCN at 65° for 5 min. Measurement is made at 645 mμ and the amount of the amino acid is ascertained from a standard graph. The oxidised form of penicillamine does not react, cysteine gives only a very faint colour (5 to 7% of that given by penicillamine), and reduced glutathione does not give any colour under the specified conditions. Krebs - Ringer bicarbonate buffer and 0·25 M sucrose do not affect the colour formation. The method is applicable to the analysis of penicillamine in Ehrlich ascites tumour cells and other tissues if the extracts are deproteinised by heating at pH 5 to 6 and 100° for 10 min.   J. N. ASHLEY

4572. Photometric determination of ketonic substances in chloramphenicol. A. Šlouf (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1959, **8** (2), 77–79.—The method is based on the reduction by the ketonic group of a mixture of tungstophosphoric and molybdophosphoric acids (Folin - Ciocalteu reagent) to molybdenum blue. *Procedure*—To 0·1 g of the sample add ethanol (1 ml) and H_2O (1 ml) and dissolve by heating on a water bath. Add the reagent (1 ml), H_2O (10 ml) and Na_2CO_3 soln. (20%) (1·5 ml) and heat for 5 min. on a boiling-water bath. Cool, dilute to 25 ml, filter, and reject the first 5 ml of filtrate. Measure the extinction of the succeeding filtrate at 610 mμ and compare with a calibration curve; 50 μg of ketonic compound can be determined in 0·1 g of chloramphenicol. *Reagent*—Dissolve $Na_2WO_4.2H_2O$ (50 g) and $Na_2MoO_4.2H_2O$ (12·5 g) in H_2O (350 ml), add H_3PO_4 (85%) (25 ml) and HCl (36%) (50 ml) and heat under reflux for 10 hr. Add Li_2SO_4 (75 g), H_2O (25 ml) and bromine (3 drops). Remove the excess of bromine by boiling, and dilute to 500 ml.   J. ZÝKA

4573. Translocation of antibiotics in higher plants. III. Estimation of griseofulvin relatives in plant tissue. S. H. Crowdy, A. P. Green, J. F. Grove, P. McCloskey and A. Morrison (I.C.I. Ltd., Akers Res. Lab., Welwyn, Herts., England). *Biochem. J.*, 1959, **72** (2), 230–241.—Methods similar to those used for the determination of griseofulvin (Crowdy *et al.*, *J. Exp. Bot.*, 1955, **6**, 371) are used for the determination of 11 compounds related to griseofulvin in bean tissue and in treating soln. They are determined spectrophotometrically after extraction from the tissues or soln. and purification by counter-current distribution and/or chromatography.   J. N. ASHLEY

4574. Polymorphism and changes of infra-red spectra of barbiturates during sample preparation. B. Cleverley and P. P. Williams (Dominion Lab., D.S.I.R., Wellington, N.Z.). *Chem. & Ind.*, 1959, (2), 49–50.—Crystalline barbiturates which contain no hydroxyl groups show spectral changes whether prepared as mulls or as potassium bromide discs; X-ray studies have shown that these changes are due to the formation of another crystalline form. This polymorphic change is induced by grinding and pressing and the presence of KBr has no effect.   K. A. PROCTOR

4575. Note on the determination of dibasic amphetamine phosphate in the presence of methyl cellulose and barbiturate. W. M. Studebaker and S. M. Wang (Southern Coll. of Pharm., Atlanta, Ga., U.S.A.). *Drug Standards*, 1959, **27** (2), 41.—Transfer the sample (containing 200 mg of dibasic amphetamine phosphate) to a Kjeldahl flask with

H_2O (200 ml), add 50% NaOH soln. (5 ml) and the anti-foam agent Velvacil 1000 (5 drops) and distil into 0·02 N H_2SO_4 (20 ml). Wash the condenser with 0·02 N H_2SO_4, dilute the combined distillate and washings to 200 ml and measure the extinction at 258 mμ.   A. R. ROGERS

4576. Determination of Largactil [chlorpromazine]. P. Spacu, E. Antonescu and C. Gheorgiu (Acad. Centr. Res., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.*, 1958, **6** (4), 573–584.—The conditions for gravimetric macro- and micro-determinations based on the use of ammonium reineckate are given. The acetone-soluble violet complex formed by chlorpromazine with $K_3[Cr(SCN)_6]$ (**I**) is used in a spectrophotometric method, the details of which are given. Details are also given of a method based on pptn. with **I** and potentiometric titration of the $[Cr(SCN)_6]^{3-}$ with $AgNO_3$ soln.   H. SHER

4577. Determination of pentazol [leptazol]. P. Spacu, I. Albescu and C. Gheorghiu (Acad. Centr. Res., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.*, 1958, **6** (4), 565–572.—A new complex $(C_6H_{10}N_4)H[Cr(NH_3)_2(SCN)_4]$ (**I**) from the interaction of leptazol with ammonium reineckate is the basis of the three proposed methods. (i) *Spectrophotometric determination*—A soln. ($\simeq$10%) of the sample is adjusted to pH 1·5 with conc. HCl. The chilled soln. is treated with a soln. of ammonium reineckate (2·5%), containing 10% of conc. HCl, until there is a slight excess. After a few minutes the ppt. of **I** is filtered off and the excess of the reagent is removed by a mixture of benzene (10 ml), ether (5 drops) and dioxan (2 drops). The ppt. is dissolved in acetone and determined in a Pulfrich spectrophotometer, with a green filter; the max. absorption is at 533 mμ. Amounts from 29 μg to 2 mg were determined with errors within the limits of the apparatus. (ii) *Volumetric determination*—This method is based on the formation of $Ag[Cr(NH_3)_2(SCN)_4]$ (**II**) and titration of the excess of Ag^+ with NH_4SCN. A soln. of the sample ($\ngtr$10% of leptazol) is treated with conc. HNO_3 to pH 1·5 to 1·6. Ammonium reineckate is added in slight excess to the chilled soln. and after a few minutes the ppt. is filtered off, the excess of the reagent being removed with the solvent mixture as before. The ppt. is dissolved in acetone and treated with an excess of $AgNO_3$. The pptd. **II** is filtered off and an aliquot of the filtrate is titrated with 0·1 N NH_4SCN, with $(NH_4)_2SO_4.Fe_2(SO_4)_3$ as indicator. (iii) *Potentiometric determination*—The excess of Ag^+ is determined potentiometrically at room temp., with a silver wire - normal calomel electrode pair.   H. SHER

4578. Determination of chloroform in aqueous pharmaceutical preparations. L. Brealey, D. A. Elvidge and K. A. Proctor (Standards Dept., Boots Pure Drug Co. Ltd., Beeston, Nottingham, England). *Analyst*, 1959, **84**, 221–225.—A gas-chromatographic method is described. By means of an injection pipette system based on that of Tenney and Harris (*Anal. Abstr.*, 1957, **4**, 2843), and described in detail, the sample is injected by the gas stream into a cup containing glass wool to trap the non-volatile components. The block supporting the cup and containing the gas inlet is heated electrically and the column, with a thermal-conductivity detector, is placed in an oil bath. The stationary phase is a high-mol.-wt. polyethylene glycol, *viz.* Carbowax 1500. Since many

samples are thick suspensions or syrups, an internal standard procedure is necessary and *n*-propanol is used because its peak appears between those of $CHCl_3$ and water. Calibration graphs are obtained by measuring the ratio of the peak heights of $CHCl_3$ and *n*-propanol, and standards containing 0·1, 0·2 and 0·4% of $CHCl_3$ and 1% of *n*-propanol in water are used. Standards and samples are chromatographed under specified conditions with N as carrier gas. Quoted results indicate satisfactory accuracy.   A. O. JONES

4579. Colorimetric assay for camphor in camphor spirit. M. I. Blake and L. V. Hopkins (N. Dakota Agric. Coll., Sch. of Pharm., Fargo, U.S.A.). *Drug Standards*, 1959, **27** (2), 39–40.—Dissolve *p*-dimethylaminobenzaldehyde (0·125 g) in H_2SO_4 (65 ml) and H_2O (35 ml). Add the reagent (7 ml) to the sample (40 μl), shake, and measure the extinction at 460 mμ after 2 hr. The procedure is much more rapid than the gravimetric assay of the U.S. National Formulary and is almost equally accurate and precise.   A. R. ROGERS

4580. Polarographic determination of cobalt, vitamin B₂ [riboflavine] and vitamin C [ascorbic acid] mixtures in tablets and ampoules. M. Sterescu, S. Arizan and M. Popa. *Rev. Chim. Bucharest*, 1959, **10** (2), 109–111.—Cobalt is determined by electro-reduction of the hexa-amminocobaltic ion after oxidation by sodium perborate in ammoniacal soln. Under these conditions riboflavine and ascorbic acid are destroyed, and the polarographic determination of Co proceeds normally. Riboflavine is extracted from the sample with an aq. soln. of Na salicylate (5%), and is then determined polarographically. Ascorbic acid is determined after dilution of the sample with acetic acid - acetate buffer soln. (pH 4·6). It was established that the other ingredients of the tablets or ampoules do not interfere, and errors are $\not> \pm 2\%$.   H. SHER

4581. Note on the assay of ethyl aminobenzoate [benzocaine] ointment N. F. X. P. J. Levine and B. F. Allen (Sch. of Pharm., Univ. of Maryland, Baltimore, U.S.A.). *Drug Standards*, 1959, **27** (2), 60.—Dissolve the sample in light petroleum and extract with several portions of aq. HCl. Cool the combined aq. phases in ice and titrate the benzocaine with $NaNO_2$ soln. The recovery of benzocaine is quantitative.   A. R. ROGERS

Food

Foods and food additives, beverages, edible oils and fats, vitamins.

4582. Chromatographic detection of hydrolysed sugar syrup in adulterated natural honey. M. Wojciechowicz and A. Andrełowicz (Dept. of Food and Feeding Hygiene, District San.-Epidemiolog. Stat., Bydgoszcz). *Chem. Anal., Warsaw*, 1959, **4** (1–2), 259–264.—Descending chromatography is carried out on Whatman No. 1 paper with the solvent system *n*-propanol - ethyl acetate - water (6:1:3). The separated components are revealed by treating the chromatogram with an acetone soln. of $AgNO_3$, drying, dipping in an ethanolic soln. of NaOH, then in aq. NH_3, washing in H_2O, immersing for 10 min. in a 15% soln. of $Na_2S_2O_3$, washing again in water and drying in air. Although the use of the solvent system named does not enable glucose and fructose to be differentiated, a constituent characteristic of natural honey, and which does not occur in hydrolysed sugar syrup, is separated (R_G 0·47). The time of development is $\simeq 44$ hr. the method is particularly useful for the serial examination of suspected samples.
            W. B. MIASKOWSKI

4583. Determination of the apparent purity of beet sugar factory juices and syrups. II. W. H. Parker (British Sugar Corp., Ltd., 134, Piccadilly, London). *Int. Sugar J.*, 1959, **61**, 9–13.—The conductance of an impure sugar soln. is practically constant at a density corresponding to $\simeq 28° \pm 2°$ Brix; soln. therefore need not be diluted to exactly 28° Brix for making conductivity measurements. An automatic diluter is described which adjusts the sugar soln. to 28° Brix and then discharges it into a cooling bath which adjusts the temp. to 20°. The soln. is then run into a copper bath, in which are suspended brass tubes containing standard sugar soln. for comparison. The electrode cell forms part of an unbalanced bridge, and conductivity measurements are taken by immersing the cell first in the standards and subsequently in the soln. under test.   E. DUX

4584. Determination of carbon dioxide in molasses. F. Durdík. *Listy Cukr.*, 1959, **75** (1), 10–11.—The vol. of the foam formed on acidifying the molasses has been compared with the CO_2 measured manometrically in a Warburg apparatus. It is stated that, in some varieties of molasses, part of the CO_2 is already liberated by the dilution with H_2O and a correction factor must therefore be used in the calculation of the manometric results.
            J. ZÝKA

4585. Amperometric determination of mercapto groups in grain proteolysis. G. I. Kotlyar (Lvov Trade-Econ. Inst., USSR). *Biokhimiya*, 1959, **24** (1), 15–18.—The determination was carried out with 0·001 N $AgNO_3$ (1 ml) in an ammoniacal medium (50 ml) containing 0·2 N aq. NH_3 and 0·2 N NH_4NO_3 (pH 9·37). The soln. was kept free from O by saturating it with N both before and during the titration. A rotating platinum electrode was used. The decrease in diffusion current after the addition of the aq. extract (1 ml) of the powdered grain was directly proportional to the decrease in concn. of Ag^+ as a consequence of the pptn. of the mercapto groups. The mercapto groups were assayed in aq. extracts of powdered grain without infusion and after a 2- and 4-hr. autolysis. Back-titration was employed to prevent both oxidation of the mercapto groups and their partial combination with NH_4^+ owing to the high pH of the ammonia buffer. Aq. extracts and protein-free filtrates of wheat, rye and barley both before and after a 96-hr. germination were investigated. The mercapto-group content increased in all cases after a 4-hr. autolysis; this was particularly marked in germinated grains.   K. R. C.

4586. Spectrophotometric determination of cholesterol in "pasta all'uovo." F. De Francesco and A. Franciosi (Lab. Chim. Provinc., Trento, Italy). *Boll. Lab. Chim. Provinciali, Bologna,* 1959, **10** (1), 57–63.—*Procedure*—Milled "pasta" (10 g) is extracted with diethyl ether for 4 hr. in a Soxhlet apparatus. After evaporation of solvent, 10 ml of a 20% KOH soln. in 70% ethanol is added, and saponification carried out. The hydrolysed soln. is transferred to a separating-funnel with H_2O (3 × 50 ml) and extracted with diethyl ether (3 × 10 ml). The ether extracts are combined and washed with 15 ml of 1% KOH soln. and then with water (3 × 5 ml). The ether layer is dried with anhyd. Na_2SO_4, then filtered and evaporated to dryness. The residue is made up to 100 ml with the reagent (0·05% $FeCl_3$ in glacial acetic acid). An aliquot of this soln. (0·5 ml) is made up to 5 ml with reagent, 3 ml of conc. H_2SO_4 is added and the extinction read after 20 min. The resulting violet colour is very stable and shows an absorption max. at 560 mμ. The results are almost free from errors due to other sterols.   L. ZANONI

4587. Experiments on the detection of preservatives using the agar diffusion test. F. Baum and H. Lamm (Inst. Ernährung, Potsdam-Rehbrücke, Berlin, Germany). *Ernährungsforschung,* 1959, **4** (1), 84–89.—The actions of benzoic, dehydroacetic and sorbic acids against the test organisms (*Rhodotorula* spp., *Penicillium* spp., *Aspergillus niger*) and baker's yeast were followed by growth on agar plates. The width of the inhibition zones for a given quantity of preservative is specific for each preservative.   J. V. RUSSO

4588. Chromatographic studies of the artificial colourings of foodstuffs. I. Column chromatography. V. Sadini (Ist. di Merceolog., Univ. di Trieste, Italy). *Chim., Milan,* 1959, **35** (1), 15–26.—A review is given of methods for determining dyes in foodstuffs, with 115 references.

II. Paper chromatography. V. Sadini. *Ibid.,* 1959, **35** (2), 81–98.—A review is given of methods for determining dyes by paper chromatography, with 158 references.   L. ZANONI

4589. Method of assessment of the genuineness of malt extract. F. Muntoni and A. Cesari (Ist. Sup. Sanità, Roma, Italy). *Boll. Lab. Chim. Provinciali, Bologna,* 1959, **10** (1), 3–11.—*Procedure*—Malt extract (10 g) is dissolved in 5 ml of boiling water. After cooling, 130 ml of 95% ethanol is added to precipitate the dextrins and the mixture is set aside for 24 hr. The ethanolic soln. is decanted, the ppt. is dissolved in 5 ml of boiling H_2O, and the dextrins are re-pptd. and the mixture is set aside for a further 24 hr. The combined ethanolic extracts are distilled at 200 mm of Hg at 65° to 70° to remove the ethanol. The residue is transferred to a 100-ml flask and 5 ml of 10% (w/v) basic Pb acetate and, after 10 min., 10 ml of satd. Na_2SO_4 soln. are added. The soln. is made up to volume, then filtered, and the polarimetric reading is made in a 2-dm cell after 1 hr. An aliquot (20 ml) of the filtered soln. is diluted to 100 ml and the reducing power with Fehling's soln. (diluted 1:4) is determined. Then maltose (%) = $[202·2\ P - (5280/R)]/41·634$, and glucose (%) = $[(13820/R) - P]/41·634$, where R is the vol. (ml) of sugar soln. required to reduce 10 ml of Fehling's soln. and P is the polarisation in a 2-dm tube. The maltose to glucose ratio is never less than 3·20 for genuine malt extracts.   L. ZANONI

4590. Use of the anthrone procedure in the carbohydrate analysis of beer. G. J. Haas and A. I. Fleischman. *Wallerstein Labs Commun.,* 1958, **21**, 139–151.—Hexose polysaccharides are quant. hydrolysed by strong H_2SO_4 in the presence of anthrone to give a green colour. The procedure based on this reaction is not affected by several factors that are troublesome in other methods. *Procedure*—De-gassed beer is diluted with water (1:250). The diluted beer (1 ml) and water (1 ml) are placed in a test-tube and 10 ml of 0·1% anthrone in H_2SO_4 (76% by vol.) is added. The mixture is shaken, heated in a boiling-water bath for 12 min., then cooled to room temp. The green colour developed is read in a photo-electric colorimeter, with a suitable filter, correction being made for the reading obtained on a water - reagent blank. For standardisation, determinations are run in the same way on a 1% aq. glucose soln. There is a linear relationship between glucose concn. and colour intensity. Tannic acid and various amino acids have no interfering action, and the presence of pentose causes only a negligible error provided that its concn. is <10% that of the hexoses. The values obtained by this procedure for total carbohydrates expressed as glucose are slightly higher than by other methods based on acid hydrolysis, owing to the loss of reducing groups in the latter cases.   J. INST. BREW. ABSTR.

4591. Differential thermal analysis of fats. I. Principle, apparatus and procedure. A. J. Haighton and J. Hannewijk (Unilever Res. Lab., Vlaardingen, Netherlands). *J. Amer. Oil Chem. Soc.,* 1958, **35** (7), 344–347.—The m.p. and polymorphic properties of various fats and oils were studied by differential thermal analysis; the curves obtained were fairly characteristic for each substance. The apparatus is fully described.

II. Melting behaviour of some pure glycerides. H. Lavery (Unilever Res. Dept., Port Sunlight, England). *Ibid.,* 1958, **35** (8), 418–422.—The melting characteristics and polymorphic transitions of 7 mono-oleyl disaturated glycerides were examined by X-ray and differential thermal analysis; results found by other workers were largely confirmed. The unstable α-forms of the glycerides were obtained by shock chilling, and other forms by heating or recrystallisation from a solvent; most of these were confirmed by X-ray analysis. Each of the 7 melting curves was distinctive. The influence of pre-melting on the apparent lowering of the initial m.p. is discussed.

P. D. PARR-RICHARD

4592. The study of animal fats in vegetable oils. G. Bigoni (Soc. Gaslini, Genova, Italy). *Olii Min.,* 1959, **36** (1), 1–4.—The method is based on the separation of the solid fatty acids as Pb salts and distillation of part ($\simeq$ 15%) of the methyl esters prepared from the liquid fraction under specified pressure and temp. The mean sap. value of the distillate is determined. The esters from olive oil have a mean sap. value of < 191; if animal fats are present (> 10%) this value varies from 194 to 212. A new value is proposed called "lower liquid acid value" (LLAV) = (SN − 190)P/100, where S is the sap. value and P the percentage of distilled ester. This value varies from − 0·6 to + 0·15, and increases when animal fats are present. Coconut oil increases this value, but this fat is detected by determination of the Wollny and Polenske numbers.   L. ZANONI

4593. Applications of spectrophotometry in the analysis of olive oil. I. Use of ultra-violet spectrophotometry for the characterisation of virgin olive oils. A. Montefredine and L. Laporta (Lab. Chim. Prov. di Pescara, Italy). *Olii Min.*, 1959, **36** (2), 31–36.—The ultra-violet spectra of various types of olive oil, and the effects of oxidation, heat and refining treatments on the absorption in the 270-mμ region are discussed.   L. A. O'NEILL

4594. Determination of tocopherol in oxidised fats. Interference from heat-formed reducing substances in highly oxidised fats. E. N. Frankel, P. M. Cooney, C. D. Evans and J. C. Cowan (U.S. Dept. Agric., Peoria, Ill.). *J. Amer. Oil Chem. Soc.*, 1958, **35** (11), 600–602.—In the determination of tocopherols in oxidised fats, the peroxides can be conveniently removed by heating the sample at 210° *in vacuo* for 15 min. if the peroxide levels are within the range 0 to 100 (by the ferric thiocyanate method). By a chromatographic procedure in which 1 g of oil in 10 ml of benzene is passed through a column (20 mm diam.) containing 1 g of silicic acid, and eluted with 50 ml of benzene (which removes the peroxides), it is shown that the heat-produced reducing substances have little effect on the tocopherol determination within the prescribed peroxide range. The presence of such substances causes an increase in darkening, viscosity, acidity and carbonyl values, with a decrease in iodine value.   G. R. WHALLEY

4595. Detection and measurement of cis-unsaturation in fatty acids. R. T. Holman, S. Euer and P. R. Edmondson (Minnesota Univ., Austin, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **80** (1), 72–79.—The method is based on measurement of the extinction of a 20% soln. of the fatty acids isolated from natural oils in CCl_4 at 2·15 μ by a base-line technique. At this wavelength, *cis*-unsaturation only is determined. Fatty acids with other types of unsaturation do not interfere, and calibration is linear with linoleic - palmitic and with oleic - elaidic acid mixtures. Results are calculated from the following expression—moles of *cis* per kg = 0·76 ($k \times 10^4$) − 0·96, where k is observed extinction per g of sample per litre. Good agreement is attained with results for *cis*-unsaturation obtained from the iodine value corrected for *trans*-unsaturation measured at 10·36 μ.   W. H. C. SHAW

4596. Analytical application of iron(III) hydroxamates. II. The determination of the esters of saturated, unsaturated, straight-chain and branched fatty acids from C_2 to C_5. W. Pilz (Organ.-anal. Lab. d. Farbenfabrik. Bayer A.-G., Leverkusen). *Z. anal. Chem.*, 1959, **166** (3), 189–193.—Previous work on the determination of esters as ferric hydroxamates (*cf. Anal. Abstr.*, 1959, **6**, 820) has been extended to a wide range of esters. It is shown that the extinctions of the ferric hydroxamate soln. at 490 mμ are approximately the same for equal concn. of ester in milli-equiv. per ml.   T. R. ANDREW

4597. Determination of vitamin A in oily solution. V. Springer (Lab. Physiol., Acad. Sci., Ivanka Pri Dunaji, Czechoslovakia). *Farmácia, Bratislava*, 1959, **28** (2), 44–50.—The losses ($\simeq 7\%$) of vitamin A during its quant. determination, due to the influence of light and air, have been studied. Most of the loss occurred during the extraction. The use of dark glass and an inert atmosphere during treatment with KOH prevents the errors. *Procedure*— To 1 g of the oil add ethanolic KOH soln. to a concn.

of 0·5 N. Boil for 15 min. under reflux in an atmosphere of N, then extract four times with peroxide-free diethyl ether; dry the extract with anhyd. Na_2SO_4, evaporate an aliquot in a stream of CO_2, dissolve the residue in spectrally pure ethanol and determine the extinction at 311, 326·5 and 334 mμ.   J. ZÝKA

4598. Qualitative and quantitative colour reaction for pyridoxal with sulphuric acid. V. E. Levine and R. N. Sass (Creighton Univ. Sch. of Med., Omaha, Nebr., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (2), 137–146.—Phenols react with aldehydes and ketones, under the influence of a condensing agent such as HCl or H_2SO_4, to give a coloured product. The analytical applications of this type of reaction are discussed and its sensitivity for various phenolic aldehydes and phenolic ketones is determined. Of the four phenolic compounds related to vitamin B_6, pyridoxol, pyridoxamine, pyridoxal (**I**) and pyridoxic acid, **I** is the only one that is also an aldehyde. Consequently the intense yellow colour that **I** yields with conc H_2SO_4 provides a selective method for its detection in the presence of the other three compounds. The reaction is sensitive to 10 μg when **I** is heated with H_2SO_4 on a water bath for 10 to 15 min. The addition of a trace of $CuSO_4$ increases the sensitivity to 1 μg. When 10 to 100 μg of **I** in 1 ml of water is mixed with 4 ml of conc. H_2SO_4 at room temp., the resulting colour, measured at 390 mμ, follows the Beer - Lambert law. A second absorption peak occurs at 335 mμ. A short review is given of analytical methods for the determination of the B_6 group and pyridoxic acid.   H. N. S.

4599. Assay and distribution of bound forms of pantothenic acid. G. M. Brown (Div. of Biochem., Dept. of Biol., M.I.T., Cambridge, U.S.A.). *J. Biol. Chem.*, 1959, **234** (2), 379–382.—A microbiological method is described for the determination of pantothenic acid, phosphopantothenic acid, pantetheine, phosphopantetheine, and coenzyme A in any one material. It depends on the differential enzymic degradation of coenzyme A and phosphopantetheine to give pantetheine, and the degradation of phosphopantothenic acid to pantothenic acid. Pantetheine is determined first on the sample by use of *Lactobacillus helveticus* and then, after the action of prostatic phosphatase, *Lb. helveticus* determines pantetheine plus phosphopantetheine. The same organism, after the action of intestinal phosphatase, determines the sum of pantetheine, phosphopantetheine, coenzyme A and dephospho-coenzyme A. Pantothenic acid is determined in the sample by means of *Saccharomyces carlsbergensis*, and this organism, after the action of prostatic or intestinal phosphatase, is used to determine pantothenic acid plus phosphopantothenic acid. Coenzyme A and dephospho-coenzyme A cannot be separated by this method.   J. N. ASHLEY

4600. Recent methods of vitamin C [ascorbic acid] determination. L. Káplár (Gen. Chem. Inst., Polytech. Univ., Budapest). *Magyar Kém. Lapja*, 1959, **14** (2–3), 122–126.—Methods, in particular those published since 1945, are reviewed. (74 references.)   G. SZABO

See also Abstracts—**4456**, Hydroperoxides in oils. **4458**, Effect of sodium borate on optical rotation of sugars. **4484**, Determination of starch. **4510**, Determination of sugars in fruits. **4580**, Determination of riboflavine and ascorbic acid in mixtures.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

4601. **Sampling and analysis of toxic vapours in the field.** E. Neale and B. J. Perry (Chem. Defence Expt. Estab., Porton Down, Salisbury, Wilts., England). *Analyst*, 1959, **84**, 226–232.—The colorimetric determination of the "nerve gases," *e.g.*, Tabun (ethyl dimethylphosphoramidocyanidate) and Sarin (*iso*propyl methylphosphonofluoridate), depends on their reaction with H_2O_2 and an aromatic base of the benzidine type in alkaline soln. In the original field method, a measured amount of air was drawn through *cyclo*-hexanol in a spined bubbler. The sample was then adjusted to 40 ml with a phosphate buffer (pH 5·5) and a suitable aliquot was treated with H_2O_2 and *o*-dianisidine soln. The pH was then raised to 11·0 by an addition of another buffer soln., the vol. was adjusted to 25 ml with an acetone - water mixture and the colour was measured in an absorptiometer. In the apparatus now described, all these operations can be effected without removal of the sample from the specially designed bubbler, the normal range being covered by the use of 0·25 to 3-cm cells in the absorptiometer. The procedure is applicable also to field measurements of Cl, $COCl_2$, CNCl and mustard gas, and probably for many other volatile toxic substances.   A. O. JONES

4602. **Determination of total gaseous pollutants in atmosphere.** P. W. West, Buddhadev Sen and Bharat R. Sant (Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chem.*, 1959, **31** (3), 399–401.—The method is based on the measurement of the thermal conductivity when small quantities of organic solvents or inorganic gases are introduced into a stream of He flowing through an empty column; a symmetrical distribution of the concn. of the solutes occurs by diffusion. The times of emergence and the areas under the curves are reasonably the same for the same quantity of a single solute or for mixtures, despite the possible differences in physical properties. Ten compounds were tested and the total error rarely exceeded 20%.
                                                      G. P. COOK

4603. **Measurement of dissolved oxygen in swamp waters. Further modification of the Winkler method.** L. C. Beadle (Makerere Univ. Coll., Kampala, Uganda). *J. Exp. Biol.*, 1958, **35** (3), 556–566.—Errors in the Winkler iodine-difference method, which are especially large with highly polluted waters, are overcome by making a preliminary clarification of a single sample from which two smaller samples are siphoned, and by the addition of iodine with the clarifying reagents to the original sample. An improved iodine titration end-point is described involving the use of a magnetic stirrer. Direct spectrophotometric determination of iodine is shown to be as accurate as, and very much more rapid than, titration, and particularly suited to the iodine-difference method. The modified method is accurate to within 0·2 mg of O per litre. With polluted water, having an oxidation - reduction potential of $< +100$ mV, 'negative' figures for the oxygen content are obtained. The cause of this is unknown but, since this potential indicates the absence of free O, the method is not thereby affected.
                                                      K. R. C.

4604. **Conductimetric analysis of natural waters. II. Determination of magnesium and anions.** G. B. Pasovskaya (Turkmen Medicinal Inst., Ashkhabad). *Zhur. Anal. Khim.*, 1959, **14** (1), 108–111.— *Determination of Mg*—Neutralise 5 to 25 ml of the water to methyl red with 0·1 N HCl, evaporate if necessary to 5 or 10 ml, adding more acid if necessary but avoiding excess, cool to 80°, add 1 drop of satd. ammonium oxalate soln. and 0·5 ml of buffer soln. of pH 10 (0·1 N aq. NH_3 - 0·1 N NH_4Cl) (1:5) dropwise with stirring to precipitate $Fe(OH)_3$ and $Al(OH)_3$ (which do not interfere), cool to room temp., dilute to 50 ml and titrate conductimetrically with EDTA (disodium salt). The results obtained agree with those of the gravimetric pyrophosphate method. *Determination of sulphates*—Neutralise the water (2 to 10 mg of $SO_4{}^{2-}$) to methyl red with 0·1 N HCl, add dry ground $BaSO_4$ ($\simeq 100$ mg) and 0·5 ml of satd. methyl violet soln., mix, add 0·5 ml of standard 0·1 N $BaCl_2$, dilute to 100 ml and titrate the excess of $BaCl_2$ conductimetrically with N Na_2SO_4. *Determination of chlorides*—Neutralise the water (2 to 20 mg of Cl^-) to methyl red with N HNO_3 and add 2 or 3 drops in excess, dilute to 25 ml and titrate conductimetrically with 0·5 N $Hg(NO_3)_2$. If a yellow cloudiness forms, prepare a fresh sample but add 6 or 7 drops of HNO_3 in excess after the neutralisation. *Determination of carbonate hardness*—In the absence of phosphates, add to the water (0·02 to 0·2 milli-equiv. of $CO_3{}^{2-}$) dry $BaCl_2$ (100 mg), 0·01 N HCl (5 ml) and 0·01 N acetic acid (5 ml); if Fe is present add NaF till the soln. is colourless or replace the acetic acid with 50 mg of citric acid; dilute to 50 ml and titrate conductimetrically with 0·1 N $Ba(OH)_2$. If phosphates are present they are first removed by adding 5 ml of 1% $BaCl_2$ soln. and filtering after 2 or 3 min. *Determination of total hardness*—Neutralise the water (0·03 to 0·06 milli-equiv. of Ca and Mg) to methyl red with HCl, boil for several minutes, adding more acid if necessary, cool to room temp., dilute to 50 ml, add 0·5 ml of buffer soln. (pH 10), and titrate conductimetrically with 0·1 N EDTA (disodium salt).   C. D. KOPKIN

4605. **Field method for the determination of uranium in natural waters.** G. H. Smith and T. R. D. Chandler (Chem. Res. Lab., Teddington, Middx., England). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/298, 11 pp.—A simple method was developed for field use in geochemical prospecting. It is based on the formation, at pH 6, of the yellow uranium - dibenzoylmethane complex which is extracted from the sample with CCl_4. The organic phase is separated from the water and its colour intensity compared with that of a set of standards. In this way it is possible to detect amounts of U equiv. to 1 μg of U_3O_8. The dibenzoylmethane is added to the water sample as a 0·5% (w/v) soln. in a 1:1 (v/v) pyridine - water mixture containing 0·6% (w/v) of EDTA (disodium salt) to complex interfering metal ions. Ascorbic acid is also added to eliminate the interference otherwise caused by Fe^{3+}. It was found that many waters contain organic matter that caused emulsification and orange - brown colours in the CCl_4 layer. To remove this interference, several types of adsorbent material were examined, including silica gel, activated alumina, kaolin, pptd. MnO_2 and several grades of activated charcoal. Of these, certain grades of activated charcoal proved to be the most satisfactory. The adsorbent is added to the acidified water sample, which is then filtered and

neutralised with alkali before proceeding with the method. It was found that the addition of 2% by vol. of silicone fluid to the CCl_4 helped to prevent emulsification, as does the addition of NaCl to the aq. phase.   NUCL. SCI. ABSTR.

4606. Determination of the phenol index of waters. F. Devlaminck (Centre Belge d'Ét. et de Document. des Eaux, 2 rue Arm. Stevart, Liége). *Bull. Cent. Belge Étud. et Docum. Eaux*, 1959, (43), 40–48.— Methods for determining phenols in water and concentrating phenols present in water in low concn. are discussed critically, and it is concluded that the most suitable are extraction with diethyl ether from $NaHCO_3$ soln. and colorimetric determination by coupling with diazotised *p*-nitroaniline. *Procedure* —When non-phenolic extractable impurities are present, the water (200 ml) is made alkaline with 20 ml of 4% NaOH soln. and the impurities are removed with ether, before proceeding with the method described. The sample of effluent water (200 ml) is acidified with H_2SO_4, and $NaHCO_3$ is added until some remains undissolved. The phenols are then extracted with ether and extracted back into 20 ml of 4% NaOH soln. The ether is washed with 10 ml of water, and the washings are added to the NaOH soln., which is then neutralised with H_2SO_4 and made up to 100 ml. The soln. (or the original water if no preliminary concentration is carried out) is treated with 2 ml of diazotised *p*-nitroaniline (10 ml of 0·75% $NaNO_3$ soln. added to 50 ml of a soln. containing 0·69 g per litre of *p*-nitroaniline in dil. H_2SO_4 immediately before use). The extinction is measured at 475 mμ within 1 hr. River waters are similarly treated with the addition of tartaric acid soln. to the sample. The preparation and standardisation with bromide - bromate of the standard phenol soln. are described, and it is recommended that they should be used within 2 hr. of preparation. It is recommended that samples of water should be made alkaline if they are to be kept for more than a few hours.   E. J. H. BIRCH

4607. Radiochemical determination of radium-C and thorium-C in radioactive springs. I. Hataye (Shizuoka Univ., Japan). *Mem. Fac. Sci., Kyushu Univ., Ser. C*, 1958, **3** (2), 63–70.—The method was designed for the determinations of radium-C (^{214}Bi) (**I**) and thorium-C (^{212}Bi) (**II**) in radon-containing carbonated mineral springs; **I** and **II** were extracted by *iso*amyl alcohol as BiI_4^-, on the addition of KI in acid soln. The respective activities of extracted **I** and **II** were measured by a Lauritsen-type electroscope; **II** was used as a tracer in the determination of **I**.   K. R. C.

4608. Radiochemical determination of radium-B and thorium-B in radioactive springs. I. Hataye (Shizuoka Univ., Japan). *Mem. Fac. Sci., Kyushu Univ., Ser. C*, 1958, **3** (2), 71–81.—The method was designed for determinations of radium-B (^{214}Pb) (**I**) and thorium-B (^{212}Pb) (**II**) in radon-containing carbonated mineral springs; **I** and **II** were extracted by a soln. of dithizone in CCl_4 (50 mg per litre) from an ammoniacal 5% KCN soln. at pH 8 to 9. To prevent interference by Po and Bi, two elimination methods were proposed. It was found that Pb is extracted preferentially from a soln. containing isotopes of Pb and Po when microgram quantities of inactive Pb are added to the soln. Bismuth was removed by washing the extracts with 0·5% KCN soln. after Pb and Bi had been extracted together. The respective activities of extracted **I**

and **II** were measured by a Lauritsen-type electroscope; **II** was used as a tracer in the determination of **I.**   K. R. C.

4609. Determination of anionic detergents in river water and sewage effluents. J. G. Slack (Southend Waterworks Co., Treatment Plant and Lab., Ulting, Maldon, Essex, England). *Analyst*, 1959, **84**, 193.—A simplification of the method of Longwell and Maniece (*Analyst*, 1955, **80**, 167) is described, the time required for a determination being considerably reduced by extraction with only one 50-ml portion of $CHCl_3$. The reagents and apparatus are as previously described (*loc. cit.*), the $CHCl_3$ layer is run into the second separating-funnel, shaken, and filtered through cotton wool. After rejection of the first 5 ml the extinction of the filtrate is measured. Results agree satisfactorily with those obtained by the longer method.

A. O. JONES

4610. Ultra-violet determination of the insect repellent diethyltoluamide. C. H. Schmidt, M. C. Bowman and F. Acree, jun. (Entomology Res. Div., Agr. Res. Serv., U.S.D.A.). *J. Econ. Ent.*, 1958, **51** (5), 694–697.—The u.v. absorption spectra of *o-*, *m-* and *p*-diethyltoluamides in 95% ethanol are plotted between 215 and 285 mμ. There are no maxima in this region and the absorptions of the three isomers are different. Calibration curves (rectilinear) are prepared for the individual isomers at 230 mμ, at concn. of from 1 to 15 μg per ml. When studying commercial samples, which vary in the proportions of the isomers, a calibration curve must be prepared from the particular lot under investigation. The amount of diethyltoluamide deposited on glass or cloth is determined by washing with ethanol and measuring the absorption of the resulting soln. at 230 mμ. Extraction of cloth with ethanol yields a small amount of other material absorbing in the same region, and high recoveries are obtained unless the material has been deposited on ethanol-washed cloth. As there is no absorption max., a constant slit width (0·66 mm) is used. There is insufficient difference in the spectra of the three isomers to calculate the relative quantities by the absorption of the mixture at three wavelengths.

E. J. H. BIRCH

See also Abstracts—**4393**, Determination of Pu in water. **4399**, Determination of F_2O in air. **4506**, Determination of ^{89}Sr and ^{90}Sr in sea water. **4616**, Water sampler.

Agricultural analysis
Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

4611. Determination of water-soluble boron compounds in soil. A. D. Gol'tman and V. G. Gurevich. *Trudÿ Khar'kovsk. Farmatsevt. Inst.*, 1957, (1), 110–114; *Ref. Zhur., Khim.*, 1959, (1), Abstr. No. 957.—The curcumin method is used. To 5 g of soil in a 25-ml flask add 10 ml of water, heat on a water bath at 50° for 30 min., shaking for 1 min. every 5 min., set aside for 20 min. at room temp. and filter. Determine B in an aliquot of the filtrate photometrically with curcumin. The presence of other substances in the aq. extract somewhat lowers the sensitivity of the determination of B; in the analysis of garden soil this error is 31%, but it is practically constant for various amounts of B

(0·2 to 1 μg) and may be allowed for. The reproducibility of the results is satisfactory; the deviation from the mean is $\pm$1·5%.   C. D. KOPKIN

4612. Comparison of polarographic and colorimetric methods for the determination of nitrates in soil. A. M. Artyushin and P. G. Kudelya. *Udobrenie i Urozhaĭ*, 1958, (7), 20–24; *Ref. Zhur., Khim.*, 1959, (3), Abstr. No. 8000.—It is established that the polarographic method may be used for the determination of NO_3^- in a soil soln. or extract. Polarograph the soln. in a basal soln. of 0·1 N HCl and 0·00066 N uranyl acetate. Construct calibration curves from standard soln. The uranyl acetate gives two waves, the first at $-0·181$ V and the second at $-0·909$ V; NO_3^- form a wave on the second uranyl acetate wave; with increasing concn. of NO_3^- the reduction potential moves in the negative direction (from $-0·9$ to $-1·1$ V). Satisfactory results are obtained with a content of NO_3^- down to 350 mg per litre. The presence of organic substances in the soil does not influence the determination of NO_3^-. The polarographic results agree well with the colorimetric data, but the polarographic method is considerably more rapid.
    C. D. KOPKIN

4613. Notes on the determination of potassium in fertilisers. J. M. Rafols Rovira (Jefe Servicios Quím. de Aprovechamientos Salineros, S.A. Barcelona). *Inf. Quím. Anal.*, 1959, **13** (1), 14–17.—The cobaltinitrite method for the determination of K_2O in fertilisers is unsatisfactory for several reasons, but the perchloric acid method is reliable and gives reproducible results.   G. H. FOXLEY

4614. Problems in the assay of chlortetracycline in feeds. A. E. Tanguay, A. B. Bogert and M. H. Blanchard (American Cyanamid Co., Pearl River, N.Y.). *Antibiot. & Chemother.*, 1959, **9** (3), 167–175.—Improved sensitivity and decreased interference from other constituents in commercial animal feeds are obtained in a three-level cylinder-plate assay for chlortetracycline (I) in animal feeds with *Bacillus cereus* var. *mycoides* ATCC 9634 as test organism. Satisfactory recovery and reproducibility were attained with $\prec$20 g of sample extracted with acidified acetone. It is concluded that, for feeds containing $>$50 g of I per ton (U.S.), the use of a blank feed is unnecessary. At 20 to 50 g per ton, blanks are generally unnecessary, but may be prepared if required by autoclaving to destroy I. The effect of minerals in high-mineral feeds is considered, and methods for obtaining satisfactory recovery of I in such samples are discussed. W. H. C. SHAW

4615. Modifications to a method for the determination of chlorinated hydrocarbon pesticide residues in plant material. G. A. Sergeant and P. B. Thompson (Dept. of the Gov. Chemist, Clement's Inn Passage, Strand, London). *Analyst*, 1959, **84**, 251–253.—The modified Stepanow procedure as previously described (*Analyst*, 1959, **83**, 335) is followed, but with $\simeq$0·1 g of Na and 0·25 g of naphthalene, and 1·5 ml of *n*-butylamine in place of the tetrahydrofuran. After reaction, the excess of Na is removed by addition of 2 ml of aq. *iso*propyl alcohol (1:1) and the *n*-butylamine is removed by heating on the water bath; a few ml of water are added and then *p*-nitrophenol as indicator and enough dil. HNO_3 to render the liquid acid. The liquid is then extracted with ether, the aq. layer is separated and its vol. is reduced to $\simeq$25 ml by heating. An aliquot ($\pm$20 ml), accurately measured, is treated with 2 ml of an $(NH_4)_2SO_4.Fe_2(SO_4)_3$ soln. (12 g and 40 ml of

HNO_3 per litre) and then with 3 ml of ethanolic Hg(SCN)$_2$ soln. (0·4%). After adjustment of the vol. to 25 ml the extinction is measured at 460 mμ and referred to a calibration graph prepared from KCl soln. treated with the colorimetric reagents. Quoted results with *pp'*-DDT, γ-hexachloro*cyclo*hexane, aldrin and dieldrin indicate satisfactory precision.   A. O. JONES

5.—GENERAL TECHNIQUE AND APPARATUS

General

4616. Battery-operated water sampler. G. E. Eden and K. V. Melbourne (Water Pollution Res. Lab., Stevenage, England). *Chem. & Ind.*, 1959, (7), 220–222.—A portable unit for collecting samples of water from open channels at intervals of 30 min. to 1 hr. consists of a number of 12-oz bottles, each of which is evacuated and connected by a rubber tube to the source from which liquid is to be drawn. When a clamp on the tube is released electromagnetically, water is forced by air pressure into the bottle. The construction and operation of the automatic sampler, which contains the dry batteries and timing unit, are described and illustrated. The apparatus can be used only when the constituent of interest in the sample is unaffected by storage in the bottles.   W. J. BAKER

4617. Reduction of micro and semi-micro weighings to normal temperature and normal pressure. C. J. van Nieuwenburg (Tech. Univ., Delft, Netherlands). *Anal. Chim. Acta*, 1959, **20** (2), 127–129.—A simple apparatus (illustrated) yields a direct reading of the correction required to reduce micro and semi-micro weighings to an N.T.P. basis, thus compensating for buoyancy variations. H. N. S.

4618. A simple ultramicro-burette. V. Habermann (Inst. Med. Chem., Charles' Univ., Pilsen, Czechoslovakia). *Chem. Listy*, 1959, **53** (1), 30–31.—A simple ultramicro-burette (illustrated) constructed on the principle of the micrometer screw enables volumes to be delivered with an accuracy of 0·00024 ml.   J. ZÝKA

4619. Aspects of organic analysis. VII. Dust-free evaporation of solutions for crystallisation on a small scale. G. W. Perold (Sect. for Coal and Tar Chem., Sci. and Res. Dept., Iron and Steel Ind. Corp. Ltd., Pretoria, S. Africa). *Mikrochim. Acta*, 1959, (2), 251–253 (in English).—With the apparatus described, soln. (1 to 4 ml) such as a fraction from a chromatographic separation or a soln. otherwise obtained can be evaporated or concentrated without creeping.   B. B. BAUMINGER

Chromatography, ion exchange, electrophoresis

4620. Detector for liquid - solid chromatography. G. Claxton (Benzole Producers Ltd., Watford, England). *J. Chromatography*, 1959, **2** (2), 136–139.—The detector consists of a section of water-jacketed capillary tubing packed with adsorbent in

which a thermocouple is embedded. When a change of composition occurs in the liquid leaving the column, a temperature change occurs in the detector owing to the change in the heat of adsorption. If the output from the thermocouple is recorded, a peak is obtained when a component leaves the column.   W. T. CARTER

4621. Improved scanner for radioactive paper strips. F. Eisenberg, jun., and I. G. Leder (U.S. Dept. of Health, Education and Welfare, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1959, **31** (4, Part I), 627–628.—A simple, easily constructed automatic paper-strip scanner is described, which gives a reproducible and strictly linear relationship between corresponding points on the chromatogram and record.   K. A. PROCTOR

4622. Calculations for a continuous gas-chromatographic (hypersorption) column. L. Szepesy and P. Benedek. *Magyar Kém. Lapja*, 1958, **13** (10–12), 369–372.—The principles and formulae for calculation are given for continuous charcoal columns suitable for separation of gas mixtures into two or three fractions. Isothermal conditions are assumed and the number of theoretical plates, the places of input and reflux and the minimal velocity of charcoal are determined by the exchange equations and equilibrium and adsorption constants. The separation of an $H - CO_2$ - acetylene mixture is described.   G. SZABO

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*See also Abstract—***4433**, Catalytic hydrogenation on paper in paper chromatography.

Optical

4623. High-temperature X-ray diffractometer. J. Spreadborough and J. W. Christian (Dept. of Metallurgy, Oxford). *J. Sci. Instrum.*, 1959, **36** (3), 116–118.—Constructional details are given of a diffractometer vacuum-furnace using a tantalum foil high-current heater and capable of operating at temp. up to 1100°. The temperature is measured by a platinum/platinum - rhodium thermocouple and can be controlled to $\pm 2°$. The instrument allows the full Bragg spectrum to be recorded while satisfying the Bragg - Brentano focusing condition.   G. SKIRROW

4624. Generally applicable semi-quantitative spectrochemical techniques. H. Svejda (Staatl. Chem.-tech. Versuchsanst., Vienna). *Öst. Chem-Ztg*, 1959, **60** (2), 37–44.—A review, with 25 references.   E. G. CUMMINS

4625. Illumination in spectrometers. M. Nordmeyer (Staatl. Materialprüfungsamt Nordrhein-Westfalen). *Arch. Eisenhüttenw.*, 1959, **30** (1), 11–13.—The effects of the field of illumination, aperture, and inlet and exit slits on the determination of line intensity and resolving power are discussed. Conditions are given under which the application of lenticular screens would be advantageous.   H. SAWISTOWSKI

4626. Use of direct-current arc in spectral analysis. Method for complete evaporation of the sample. M. Malínek (Inst. of Metall., Acad. Sci., Prague). *Chem. Listy*, 1959, **53** (2), 145–153.—The principle of the method is given, with a survey of published communications dealing with its use. (29 references.)   J. ZÝKA

4627. Improved method of introducing [powdered] samples [into the arc] in spectrographic analysis. O. F. Chesnokov and Yu. A. Kopelkin (Comprehensive Geophysical Expedition Sibreofiztrest). *Zavod. Lab.*, 1958, **24** (12), 1487–1489.—An electromagnetic vibrator is described.   G. S. SMITH

4628. Isotopic analysis by interferential spectrometry. J. Artaud and S. Gerstenkorn (Commissariat à l'Énergie Atomique, Paris). Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Rep. A/CONF.15/P/328, 20 pp.—The principle of isotopic analysis by emission spectroscopy is discussed. The method is valid only for those elements where the isotopic displacement has a value twice as large as the Doppler broadening. The Fabry - Perot photoelectric spectrometer used for isotopic analysis is briefly described. The application of this method to the isotopic analysis of He, Li, Pb and U is described.   NUCL. SCI. ABSTR.

4629. Universal buffer solution for use in ultraviolet spectrophotometry. M. T. Davies (British Drug Houses Ltd., Graham St., London). *Analyst*, 1959, **84**, 248–251.—Owing to the high light-absorbing properties of phenylacetic and diethylbarbituric acids, the buffer soln. of Prideaux and Ward (*J. Chem. Soc.*, 1924, **125**, 426) and Britton and Robinson (*Ibid.*, 1931, 458) require modification before they can be used in u.v. spectrophotometry. Aq. soln. of tri(hydroxymethyl)methylamine possess high uniform transmittance, and this base was found to be a suitable substitute for the barbitone of Britton and Robinson's mixture. The composition of the modified buffer soln. is given, and the pH values of liquids prepared by addition of 0·4 N HCl or 0·4 N NaOH to 50 ml of this soln. and dilution to 200 ml are tabulated. The values range from pH 2 to pH 12 and have been determined at 25° and at 37°. Ionic strength, dilution and buffer capacity data for these soln. are provided.

A. O. JONES

4630. Potassium bromide discs for mounting Nujol mulls. Han Tai and A. L. Underwood (Dept. of Chem., Emory Univ., Atlanta, Ga., U.S.A.). *Chemist Analyst*, 1958, **47** (4), 104.—Nujol (liquid paraffin) mulls for i.r. spectroscopy are prepared by placing the sample (2 mg, 200 mesh) on the centre of a potassium bromide disc (200 mg, 0·5 in.), adding a drop of liquid paraffin ($\simeq 0\cdot 1$ ml), covering with another disc, and rubbing the discs together to obtain a uniform mull. The disc sandwich is then mounted in a holder for examination. Alternatively, the sample may be mulled with a pestle and mortar, a drop of the mull placed between two discs and the discs moved about to give a uniform sample layer. The discs are rejected after use, and liquid paraffin spilled on the disc holder can be removed with CCl_4. This method gives spectra comparable in quality with those given by other mull methods.

R. E. ESSERY

4631. High-resolution infra-red grating spectrometer. National Bureau of Standards (Washington, D.C., U.S.A.). *Appl. Spectroscopy*, 1958, **12** (6), 175–176.—The spectrometer described provides extremely high resolution in the 3 μ to 6-μ region and can be used either as a single-pass or double-pass instrument. A special drive mechanism allows it to scan small portions of a rotational - vibrational band either quickly or slowly so that not only are the rotational lines resolved but the fine-structure

splitting of individual lines can be detected. By recording the absorption spectra simultaneously with the calibrated fringe system of a Fabry - Perot interferometer, wavelengths can be measured to 1 part in 5×10^5.

K. A. Proctor

4632. Use of crystals of silver chloride in infra-red spectrography. Mlle Le Sech. *Chim. Anal.*, 1958, **40** (11), 425–429.—The advantages and disadvantages of the use of crystals of AgCl as transparent plates in the i.r. region beyond 9μ are discussed. The material is sufficiently transparent from 0.6 to 25μ and is resistant to acids, H_2O, CS_2 and hydrocarbon solvents. Its disadvantages are its high index of refraction, high ductility, ease of reduction by metals with which it comes in contact, sensitivity to visible and u.v. light, solubility in aq. NH_3 and other complexing agents, and high price. A special technique of pressing between perfect optical surfaces of plate glass or stainless steel is described, as normal polishing methods scratch it very easily. Examples of its use are given. The possibility of using thallium iodobromide is discussed.

E. J. H. Birch

4633. Improved measuring apparatus for X-ray absorption spectrometry. H. P. Hanson, W. E. Flynt and J. E. Dowdey (Dept. of Physics, Univ. of Texas, Austin, U.S.A.). *Rev. Sci. Instrum.*, **29** (12), 1107–1111.—Two methods of data-taking which eliminate the need for a stabilised X-ray power supply are described. In the first, the sample is oscillated in and out of the beam with a period small compared to drift. From the observed I and I_0 a quantity proportional to the absorption coefficient is electronically calculated and plotted. In the second, two counters are arranged in tandem with the sample between them, yielding I and I_0 simultaneously.

G. Skirrow

4634. X-ray spectrographs for rapid X-ray fluorescence analysis with photographic recording. E. F. Priestley (Min. of Supply, A.R.D.E., Fort Halstead, Kent, England). *J. Sci. Instrum.*, 1958, **35** (11), 409–413.—Curved-crystal spectrographs are described covering the range from K to U. The simultaneous recording of spectra between 0.5 and 2.5 A or 1.5 and 3.75 A is possible, and minor constituents (0.1%) can be detected. In more sensitive spectrographs (0.001%) a scanning device is used for covering the required wavelength range.

G. Skirrow

4635. Effect of variations in ambient temperature upon the optical alignment of an X-ray fluorescence spectrometer. T. A. Davies (Mond Nickel Co., Ltd., Birmingham, England). *J. Sci. Instrum.*, 1958, **35** (11), 407–409.—The influence of temperature on the dispersion of an X-ray fluorescence spectrometer has been attributed to changes in the interplanar spacing of the diffracting crystal.

G. Skirrow

4636. Differential refractometer. P. Kratochvíl and B. Sedláček (Phys. Chem. Dept., Chem. Inst. Acad. Sci., Prague). *Chem. Listy*, 1958, **52** (12), 2414–2416.—The suggested autocollimation arrangement enables a lens of large focal length to be used without lengthening the apparatus. The two-part tube permits the simultaneous control of the zero position as well as the location of the image. The accuracy can thus be increased. The light from the source passes through the filter and the rays are reflected from a small mirror to the axial direction of the apparatus. After passing through the objective (110 cm focal length), the rays pass through a tube, are reflected from the mirror and again pass through the tube. The tube and mirror are placed in a double-jacketed protective vessel thermostatically controlled with H_2O. The arrangement can be used for measurements of differences in the range of 1×10^{-2} units with an accuracy of $\pm 0.1\%$.

J. Zýka

4637. Automatic control of liquid composition based on variations of refractive index. H. Koropecká and J. Koropecký (Inst. Chem. Engng, Sch. of Chem. Technol., Prague). *Chem. Průmysl*, 1958, **8** (12), 640–641.—The described method is based on the observation of the change of focal length of the lens-shaped tube through which the liquid flows. The sensitivity of this arrangement has been tested with sugar soln. of different concn. and it is claimed that the apparatus can be used for measurements of n_λ^t with an accuracy $>2.5 \times 10^{-4}$ and that the relation between n_λ^t of the liquid and the response of the recorder is linear within a range of 0.0800 unit of refractive index. The apparatus can be adapted for the automatic control of production processes.

J. Zýka

4638. Microscope attachment for accurate microdrilling and the removal of analytical samples from small areas. A. C. Simon and D. A. Gildner (U.S. Naval Res. Lab., Washington, D.C.). *Rev. Sci. Instrum.*, 1958, **29** (12), 1125–1128.—The air-driven micro-drill which can use drills as small as 0.001 in. in diam. is interchangeable with a microscope objective and can be adjusted to work an area centred under the cross-hairs of the objective. The drilling process is observed from an auxiliary stage with a low-power microscope, and the feed of the drill is controlled by the microscope fine-adjustment.

G. Skirrow

4639. Ring-oven drop colorimetry with the aid of a standard silver sulphide scale. H. Weisz, M. B. Čelap and V. V. Almažan (Inst. f. anorg. u. allg. Chem., Techn. Hochsch., Vienna). *Mikrochim. Acta*, 1959, (1), 36–43.—Factors are given for the semi-quant. evaluation of the sulphide rings for 14 ions obtained by the ring-oven technique. The metals are fixed as sulphides, then converted into Ag_2S, and the intensity of the ring is compared against a set of standards produced by heating a series of CuS rings with 1% $AgNO_3$ soln.

T. R. Andrew

Electrical

4640. Use of the pool cathode in polarography. R. C. Rooney (Brit. Cast Iron Res. Ass., Bordesley Hall, Alvechurch, Birmingham, England). *Talanta*, 1959, **2** (2), 190–194.—A cell of the conventional H type is illustrated, in which the difficulty of ensuring close reproducibility of the pool size is overcome by forming the pool in a glass cup, which is filled to overflowing every time the pool is used. The advantages and disadvantages of this cell for conventional and cathode-ray polarography are discussed, and comparative results are quoted for three reactions in which the pool and dropping mercury electrodes are used. In conventional polarography, the pool electrode gives a gain in sensitivity by a factor of 20 over the dropping

mercury electrode, but the fact that a repeat polarogram cannot be run renders it unsuitable for this type of instrument. In cathode-ray polarography, the pool electrode offers some advantages over the dropping mercury electrode, the main disadvantage, that each cell must be individually calibrated, or the same cell used throughout, being less serious because this type of instrument produces polarograms every 7 sec. with a pool cathode, the peak height being reproducible for 20 to 30 sweeps, which is ample time for measuring the height.   R. E. Essery

4641. Construction and characteristics of Teflon-covered polarographic electrode for intra-vascular oxygen determination. J. Krog and K. Johansen (Univ. Inst. for Exp. Med. Res., Ullevål Hosp., Oslo, Norway). *Rev. Sci. Instrum.*, 1959, **30** (2), 108–109.—The Teflon membrane shows a high permeability to O and can be heat-sterilised without damage. It shows good mechanical strength and is resistant to surface adhesions of proteins. It must be free from pinholes, so that only cast Teflon film is satisfactory.   G. Skirrow

4642. Use of the rotating platinum micro-disc electrode in polarographic analysis. M. B. Bardin, Yu. S. Lyalikov and V. S. Temyanko (Kishinevsk State Univ.). *Zhur. Anal. Khim.*, 1959, **14** (1), 24–27.—Distinct polarographic waves of good reproducibility were obtained for O, H$^+$, [AuCl$_4$]$^-$ and [PtCl$_6$]$^{2-}$ with the rotating platinum micro-disc electrode, in 0·1 N NaNO$_3$ as basal soln. In 10 readings (without cleaning the electrode) the max. deviation from the average was $\not> 3\%$. For accuracy and reproducibility the electrode must be accurately centred. The Levich equation was used in the calculations—

$$i_d = 0.62 \ nFD^{2/3}\omega^{1/2}v^{-1/6}cS,$$

where i_d is the diffusion current, n is the number of electrons transferred in the reaction, F is Faraday's number, D is the diffusion coeff. in sq. cm per sec.; ω is the angular velocity of rotation ($= 2\pi m$, where m is the number of revs. per sec.), v = kinematic viscosity of the liquid in sq. cm per sec., c is the concn. of reducing ion in moles per litre, and S is the electrode surface area in sq. cm. The values of i_d found for H$^+$ in a soln. 4×10^{-4} N in HCl in a basal soln. of 0·1 N NaNO$_3$ differed from the calculated values in 5 experiments at different ω by 10·5 to 18·0%, which was considered satisfactory agreement under the conditions used; S was 0·78 sq. mm. By using the Levich equation, the diffusion coeff. of [AuCl$_4$]$^-$ in 0·1 N NaNO$_3$ was calculated as 1·2 $\times$ 10^{-5} sq. cm per sec.   C. D. Kopkin

4643. Transistorised switch for derivative polarography. J. Krugers (Lab. for Anal. Chem., Univ. of Amsterdam, Holland). *Anal. Chem.*, 1959, **31** (3), 444–447.—An electronic device is described to replace mechanical switching. The circuit may also be used for converting a small d.c. into an a.c. of any desired frequency between 0·1 cycle and 10 kilocycles per sec.   H. F. W. Kirkpatrick

4644. Automatic titrimetry: a simple apparatus for recording full-scale potentiometric titrations. J. Haslam and D. C. M. Squirrell (I.C.I. Ltd., Plastics Div., Welwyn Garden City, Herts., England). *J. Appl. Chem.*, 1959, **9** (2), 65–68.—The apparatus described consists of three main parts—(*i*) an injection delivery system (with hypodermic syringes of vol. 1, 5, 10 and 20 ml) that

delivers titrant at a definite rate, (*ii*) a system indicating the change of pH or e.m.f. produced by the titrant, and (*iii*) a recorder with variable resistance to cover a range of 0 to 10 pH units or 0 to 50 mV. The chart speed of the recorder is 1 in. per min. High accuracy was attained in the following titrations—sebacic acid in nylon-610 salt cross-decomposed with N HCl; H$_3$PO$_4$ with NaOH soln.; chlorides; mixtures of chloride and bromide; amines with HClO$_4$ in glacial acetic acid; boric acid - mineral acid mixtures with NaOH; poly(methacrylic acid) in methyl methacrylate - methacrylic acid copolymers; salicylic acid in phenyl salicylate; and V^{3+} titrated with 0·02 N 2(NH$_4$)$_2$SO$_4$.Ce(SO$_4$)$_2$.2H$_2$O. The calibration of the hypodermic syringes should be checked frequently, whilst the titrant soln. should be standardised against a known amount of pure compound.
                                        W. J. Baker

4645. Potentiometric micro-titration apparatus. I. D. P. Wootton (Post-grad. Med. Sch., Hammersmith Hosp., London). *Lab. Practice*, 1959, **8** (1), 11–13.—The titration assembly and electronic potentiometer described and illustrated are used for the routine determination (by AgNO$_3$ titration) of Cl$^-$ in samples (0·1 or 0·2 ml) of plasma, serum, urine, or other fluids, by the method of Sanderson (*Biochem. J.*, 1952, **52**, 502). Reproducibility is within 1 milli-equiv. per litre for plasma levels of $\simeq$ 100 milli-equiv. per litre. The values obtained are claimed to be the true content of Cl$^-$, those obtained by the Van Slyke method being low by 2 to 3 milli-equiv. per litre.   W. J. Baker

4646. Anodic chronopotentiometry at solid electrodes. Precision as a function of transition time for some organic compounds. J. D. Voorhies and N. H. Furman (Frick Chem. Lab., Princeton Univ., N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (3), 381–384.—A simple oscillographic method involving Polaroid photographic recording has been used to measure short transition times in chronopotentiometric analyses and has shown that certain time-dependent errors can be eliminated by using such short transition times.   K. A. Proctor

4647. Use of dibromohydroxyquinoline in amperometric titration. L. I. Panteleeva. *Nauch. Zap. L'vovsk. Politekh. Inst.*, 1958, (50), 50–56; *Ref. Zhur., Khim.*, 1959, (5), Abstr. No. 15,075.—The titration of Fe, Cu and Ti with a dropping mercury cathode is based on the pptn. of these metals with an acid soln. of 35% 5 : 7-dibromo-8-hydroxyquinoline (**I**) in acetone. Titration of Cu and Fe is carried out without the application of an external e.m.f.; the reducing current is applied to a metal soln. at 50°, containing 10% (v/v) of acetone and 1% gelatin soln. (2 to 3 drops); there is no preliminary removal of O. Mercury is extracted from the soln. with a small amount of CHCl$_3$. Titration of > 0·04 mg of Fe per 10 ml in 0·01 to 0·02 N HCl or H$_2$SO$_4$ is not affected by alkali metals, alkaline-earth metals, Be, Mn, Al, Cr, As, Sb, Sn, Cd, Zn or Hg, as these are not pptd. by **I** in acid medium; Ti is complexed with tartaric or citric acid; Cu and V do not interfere. Copper is titrated in 0·01 to 0·05 N HCl or H$_2$SO$_4$; a 300-fold excess of Al does not affect the titration; > 0·5 mg of Cu in the presence of < 20 mg of Fe can be titrated in the presence of ammonium oxalate (5 mg for each mg of Fe) at pH 2 to 4 with an accuracy of $\simeq$2%. *Procedure for Cu in aluminium alloys*—Dissolve the sample (0·5 to 1 g) in HCl (30 ml) or in HNO$_3$ (1 : 1) (1 ml)

evaporate almost to dryness, dissolve in H_2O and make up to 100 ml with H_2O; to a 2 to 5-ml aliquot in the titration vessel add a little $CHCl_3$, acetone (1 to 2 ml) and 1% gelatin soln. (2 to 3 drops) and make up to 15 ml with ammonium oxalate soln. (2 g in 100 ml of $0.1 N$ HCl); place in a thermostat at 50° for 10 min. and titrate with **I**. The determination takes 90 min.   *Procedure for Ti*—Determine Ti by back-titration of an excess of **I** with a copper soln.   Make the test soln. 0.01 to $0.015 N$ with respect to HCl or H_2SO_4 and 10% with respect to acetone, heat to 50° to 60°, add a soln. of **I** dropwise with stirring and, when the $TiO_2(C_8H_4Br_2ON)_2$ is completely pptd., add an excess of **I** (2 to 3 ml) and back-titrate amperometrically with standard copper soln.   If the concn. of acetone in the soln. is > 30% add hot $0.1 N$ HCl.   K. R. C.

4648. Activation analysis for industries.   A. De Haan, jun. (Tracerlab, Inc., Richmond, Calif.). *A.S.T.M. Special Tech. Publ.*, 1958, (215), 54–61.— The basic principles and techniques of activation analysis are discussed.   Applications are cited to the analysis of trace concn. of chemical elements in metals and alloys, in chemicals, petroleum, food, plastics and other industrial products.

CHEM. ABSTR.

4649. Radiochemical tracer analysis.   A new approach resulting in increased accuracy.   D. A. Lambie (U.K.A.E.A., Radiochem. Centre, Amersham, Bucks., England). *Analyst*, 1959, **84**, 173–176.—It is shown that the errors inherent in radioactive tracer analysis may be reduced by measuring the radioactivity of the unseparated fraction (*i.e.*, the filtrate) rather than that of the separated fraction (*i.e.*, the ppt.).   A satisfactory application to the determination of Co in the presence of Ni is described.   A. O. JONES

4650. Particle-size analysis by gamma-ray absorption.   C. P. Ross (Savannah River Lab., E. I. du Pont de Nemours & Co., Inc., Aiken, S.C., U.S.A.). *Anal. Chem.*, 1959, **31** (3), 337–339.—The concn., at a fixed depth, of uranium oxide particles settling from a uniform suspension was continuously determined by measuring the transmittance of γ-rays from a ^{241}Am source.   For the particles tested, the absorption of γ-rays depended only on the mass of suspended material, and the data obtained were converted to a standard curve of particle fractions below a certain size *vs.* the diameter obtained from Stokes's law.   The fraction undersize was determined with a 95% confidence limit of $\simeq \pm 0.04$ and the average diameter according to Stokes's law was determined to about $\pm 0.3 \mu$.   The method is applicable to particles up to 74 μ in diameter that have an absorption coeff. significantly different from that of the suspending medium.

K. A. PROCTOR

4651. Rapid analysis of unknown mixed γ-emitters with a γ-ray scintillation spectrometer.   Fumio Aoki, Seishi Yajima and Toshio Kurosawa (Japan Atomic Energy Res. Inst., Tokai, Ibaragi-ken). *Japan Analyst*, 1958, **7** (11), 695–699.—Fission products were fractionated by the ion-exchange-resin method (Cohen *et al.*, *Nucleonics*, 1948, **3**, 22; Thompkins *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 2969) and each fraction was examined with a γ-ray scintillation spectrometer for the approx. amount of each fission product to be determined.

K. SAITO

4652. Note on a possible source of error in counting radioactive samples.   G. Saucier and L. P. Dugal (Dept. Biol., Univ., Ottawa, Ont.). *Canad. J. Biochem. Physiol.*, 1959, **37** (5), 721–722.—In the course of an experiment in which ^{14}C was incorporated into the cholesterol in different tissues, a loss of activity occurred when samples of digitonide were re-counted some hours later.   This effect is ascribed to the natural radioactivity present on atmospheric dust.   N. E.

4653. Method and apparatus for analysing mixtures of gaseous materials by composition modulation.   Esso Research and Engineering Co. Brit. Pat. 814,317; date appl. 25.4.56.   U.S.A., date appl. 20.5.55.—The key component in a stream of a (binary) mixture of gaseous materials is determined by passing the stream at const. temp. into an adsorber in which the pressure is varied cyclically, between predetermined upper and lower limits, for a time period, at each pressure, sufficient for the adsorbent to reach an equilibrium capacity for the key component, so that its content is cyclically and alternately modulated to decrease the content at the higher pressure and increase it at the lower pressure.   The range of modulation of the key component in the stream is detected and electrically indicated with reference to that of an identical stream containing a known amount of the key component.   J. M. JACOBS

4654. Combustible-gas analysers for high-temperature operation.   N. W. Hartz. *Instrum. Control Systems*, 1959, **32** (6), 886–887.—An instrument is described for continuous monitoring of inflammable vapours in ovens drying coated fabrics, abrasive products, brake linings, cast plastic films, etc.

N. E.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	A
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
crystalline	} cryst.
crystallised	
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA

milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_v
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm.
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\not>$	not less than	$\not<$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

ANALYTICAL ABSTRACTS

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